The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Thermodynamic Study of the System Sodium Sulfite–Sodium Bisulfite–Water at 25°C.

Robert S. Morgan

June, 1960

A THERMODYNAMIC STUDY OF THE SYSTEM SODIUM SULFITE-SODIUM BISULFITE-WATER AT 25°C.

A thesis submitted by

Robert S. Morgan

B.Ch.E. 1952, Rensselaer Polytechnic Institute
M.S. 1956, Lawrence College

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1960

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INTRODUCTION AND PRESENTATION OF THE PROBLEM

Solutions of electrolytes are of great importance both in research and industry. For example, the pulp and paper industry uses thousands of tons of electrolytes daily in its processes. Even though these processes are operating successfully today, improvements and radical changes in present processes may be needed for successful operation tomorrow. The pursuit of many possible approaches to new and better processes is blocked or greatly hindered by the lack of fundamental data.

One of the key pieces of fundamental information about an electrolyte solution is its composition in terms of the specific constituents present in the solution under a given set of conditions. For simple electrolytes like sodium chloride in aqueous solution, this is no problem. However, there are many electrolytes which undergo chemical reactions in solution; in this case the composition of such a solution at equilibrium depends upon the various chemical equilibria involved. For example, a solution of presumably pure sodium bisulfite is known to have an appreciable vapor pressure of sulfur dioxide above it. Therefore, sodium bisulfite in solution must undergo a chemical reaction which produces sulfur dioxide. It also follows that at equilibrium a sodium bisulfite solution is composed of several constituents in equilibrium with each other. There is no known analytical method whereby the composition of a sodium bisulfite solution can be ascertained. However, the equilibrium composition can be calculated from certain basic thermodynamic data. This is only one example of many electrolytes that undergo

chemical reaction in solution in the process liquors of the pulp and paper industry. Indeed many of the process liquors contain more than one family of constituents in chemical equilibrium with each other.

The problem of the composition of a supposedly pure sodium bisulfite solution is a portion of the over-all problem of the composition of the system sodium sulfite-sodium bisulfite-water. The program of this thesis was a thermodynamic study of the system sodium sulfite-sodium bisulfite-water with the objective of obtaining sufficient thermodynamic data to permit the composition of the solutions at equilibrium to be determined. The data required are the thermodynamic properties of sodium sulfite, sodium bisulfite, sulfur dioxide and water in the various solutions of the system in terms of activity, activity coefficients or fugacity.

The activity coefficients of single electrolytes in aqueous solution not involving chemical reaction have been studied for many years. Thus, there are considerable data in the literature for the activity coefficients of salts such as sodium chloride in aqueous solution. The activity coefficients of the constituents in some solutions of mixed electrolytes not involving chemical reaction have also been studied. There is a fair amount of activity coefficient data on mixtures such as sodium chloride-potassium chloride in aqueous solution. No work was found in the literature giving activity or activity coefficient data on systems containing mixed electrolytes involving chemical reaction. The system sodium sulfite-sodium bisulfite-water is an example of a mixed electrolyte solution involving chemical reaction.

There is a certain amount of activity-coefficient data in the literature of importance to present processes of the pulp and paper industry. Activity coefficients of the following compounds as single solutes in aqueous solution have been obtained experimentally (1): sodium carbonate, sodium hydroxide, sodium sulfate, sodium thiosulfate and magnesium sulfate. Some of these data are available over a range of temperatures. Of particular note are the data on sodium carbonate of Taylor (2). He determined the activity coefficients of aqueous sodium carbonate over a range of temperatures from 15 to 95°C. The only activity-coefficient data on mixtures are a very limited amount of data for the activity coefficients of sodium hydroxide in sodium sulfate solution. There is a significant contribution by Han and Bernardin (3). These authors have calculated, using simplifying assumptions, the activity coefficients of sodium bicarbonate in aqueous solution from Taylor's data for sodium carbonate and other data available in the literature. Busche (4) has shown that these calculated activity-coefficient data for sodium bicarbonate are consistent with those derived from measurements of the pH of sodium carbonate-bicarbonate solutions and the solubility of sodium bicarbonate in sodium carbonate-bicarbonate solutions. No activity or activity-coefficient data were found in the literature for the system sodium sulfite-sodium bisulfite-water.

The fugacity of water and sulfur dioxide can be evaluated from vapor-pressure data. Johnstone, et al. (5) have measured the vapor pressures of water and sulfur dioxide above certain sodium sulfite-bisulfite mixtures at several temperatures from 35 to 90°C. His data

have an accuracy of about 5% and have proven useful for characterizing the equilibrium vapor pressures of this system. Kotzerke (6) reports vapor-liquid equilibria for the system sodium hydroxide-sulfur dioxide-water, over a range of composition that includes both sulfite-bisulfite mixtures and bisulfite-sulfurous acid mixtures. The data cover a very limited range of dilute concentrations and are given for 10, 30 and 65°C.

The over-all objective of this thesis then was to make a thermodynamic study of the system sodium sulfite-sodium bisulfite-water. The final goal of the thesis was to determine the equilibrium composition of this system. An experimental program was pursued to obtain thermodynamic data which, together with data available in the literature, were sufficient to determine the composition. Activity-coefficient data for sodium sulfite and sodium bisulfite, and activity data for water were determined from isopiestic vapor-pressure measurements together with dynamic gas saturation vapor-pressure measurements. Fugacity data for sulfur dioxide in the case of sodium bisulfite solutions were determined from the dynamic vapor-pressure measurements. Fugacity data for sulfur dioxide in the case of sodium sulfite-bisulfite mixtures were estimated from Johnstone's date (5). All measurements were made at 25°C.

NOMENCLATURE

$\underline{a}$	activity
$\underline{A}$	constant in the Debye-Hückel equation
$\underline{A}'$	new value of A
$\underline{b}$	limiting slope in the Debye-Hückel equation
$\underline{B}$	constant in the Debye-Hückel equation
$\underline{B}'$	new value of B
$\underline{D}$	logarithmic ratio of activity coefficients, log $(\gamma_1/\gamma_{1\ (\underline{r})})$
$\underline{D}_c$	value of the logarithmic ratio of activity coefficients calculated from Equation (15)
$\Delta\underline{D}$	defined as $\underline{D} - \underline{D}_c$
$\underline{f}$	fugacity
$\underline{F}$	free energy of Gibbs
$\underline{H}$	Henry's law constant, moles/1000 g.-atm.
$\underline{I}$	ionic strength defined by Equation (10)
$\underline{k}$	quantity defined by Equation (24)
$\underline{K}$	equilibrium constant defined by Equation (3)
$\underline{K}_H$	hydrolysis constant defined by Equation (19)
$\underline{K}_1$	first ionization constant of sulfurous acid
$\underline{K}_2$	second ionization constant of sulfurous acid
ln	logarithm to the base $\underline{e}$
log	logarithm to the base 10
$\underline{m}$	molality, moles/1000 g. solvent
$\underline{m}_{Na}$	molality of total sodium in a system
$\underline{n}$	number of moles of a constituent in a system

p vapor pressure, atmospheres

x the fraction of the total ionic strength contributed by a given constituent when used with a subscript

x degree of hydrolysis when used without a subscript

z valence

γ molal activity coefficient

μ chemical potential defined by Equation (36)

μ° chemical potential in some arbitrary standard state

ν total number of ions produced by the dissociation of one molecule of an electrolyte

ν_+ number of cations produced by the dissociation of one molecule of an electrolyte

ν_- number of anions produced by the dissociation of one molecule of an electrolyte

Subscripts:

aq aqueous

i an ionic species

l liquid

r solution used as lower limit of integration in Equations (8) and (12)

R reference electrolyte

S sulfur dioxide

w water

$\pm$ a mean ionic quantity

1 sodium sulfite

2 sodium bisulfite

$1,2\cdots c$ constituents of a system

THERMODYNAMICS OF THE SYSTEM SODIUM SULFITE-SODIUM BISULFITE-WATER

DEVELOPMENT OF THE EQUILIBRIUM EQUATION

The system sodium sulfite-sodium bisulfite-water is a part of the general system sulfur dioxide-sodium hydroxide-water. When sulfur dioxide is added to an aqueous solution of sodium hydroxide, the initial reaction is

$$2\ NaOH_{(aq)} + SO_{2(aq)} = Na_2SO_{3(aq)} + H_2O_{(l)} \qquad (1)$$

There is an equivalence point, called the first equivalence point, at a pH of about 10. At this equivalence point it is generally assumed that Equation (1) is displaced virtually completely to the right and that the solution is essentially a pure sodium sulfite solution.

If the addition of sulfur dioxide is continued past the first equivalence point, further reaction takes place as described by the following equation:

$$Na_2SO_{3(aq)} + SO_{2(aq)} + H_2O_{(l)} = 2\ NaHSO_{3(aq)} \qquad (2)$$

There is an equivalence point, called the second equivalence point, for this reaction at a pH of about 4. It is the general system described by Equation (2) bounded by the two equivalence points that defines the specific system sodium sulfite-sodium bisulfite-water.

This equation elucidates the composition of a sodium bisulfite solution, the example cited in the introduction. The observation that there is a vapor pressure of sulfur dioxide above sodium bisulfite

solutions indicates that Equation (2) is not displaced completely to the right and that a sodium bisulfite solution contains sodium sulfite, sodium bisulfite, dissolved sulfur dioxide and water. It should be noted that in addition to the specific constituents indicated by the equation, there are small amounts of hydrogen, hydroxyl and bisulfite ions present in the solution governed by the dissociation of the dissolved sulfur dioxide (sulfurous acid) and water. It is evident that the reaction expressed by Equation (2) is important in determining the composition of the entire sodium sulfite-sodium bisulfite-water system.

The system sodium sulfite-sodium bisulfite-water can be defined in terms of the total sulfur dioxide and total sodium in the system. If sulfur dioxide, sodium hydroxide and water are placed together in a closed vessel with an inert gas, nitrogen, at 25°C. and a total pressure of one atmosphere, there will be two phases present. The Gibbs' phase rule states that such a system will have four independent variables. Two of these independent variables have already been specified—the temperature and the total pressure. Thus, the other two independent variables could be chosen as the total sulfur dioxide and the total sodium. However, it is more convenient to choose these other two independent variables as the total sodium and the ratio of total sulfur dioxide to total sodium. The four independent variables thus chosen for this study were the total sodium, the ratio of total sulfur dioxide to total sodium, a total pressure of one atmosphere, and a temperature of 25°C. In the case of sodium sulfite-bisulfite mixtures, the total sodium is expressed in terms of the total ionic strength.

The system sodium sulfite-sodium bisulfite-water has already been defined by means of the equivalence points of the reactions described by Equations (1) and (2). It is evident from Equation (1) that the first equivalence point occurs when the ratio of total sulfur dioxide to total sodium is 0.5; also, it is evident from Equation (2) that the second equivalence point occurs when the ratio of total sulfur dioxide to total sodium is 1.0. Thus, the system sodium sulfite-sodium bisulfite-water is also defined as the system sulfur dioxide-sodium hydroxide-water when the ratio of total sulfur dioxide to total sodium has values from 0.5 to 1.0. There are three terms commonly used to define portions of these systems. When the ratio of total sulfur dioxide to total sodium is: 1) 0.5, the system is called a "sodium sulfite solution"; 2) 1.0, the system is called a "sodium bisulfite solution"; 3) between 0.5 and 1.0, the system is called "sodium sulfite-bisulfite mixtures" or "sodium sulfite-bisulfite solutions".

It is evident from the preceding discussion that the chemical reaction described by Equation (2) is the main one to be considered in the system sodium sulfite-sodium bisulfite-water. The equilibrium equation for this reaction is[1]

$$K = \frac{\underline{a}_2^2}{\underline{a}_1 \, \underline{a}_S \, \underline{a}_W} = \frac{\gamma_2^4 \, \underline{m}_2^2}{\gamma_1^3 \, \underline{m}_1 \, \underline{a}_S \, \underline{a}_W} \qquad (3)$$

[1] Derivations of the thermodynamic relationships used are given in Appendix VIII. They are also presented in numerous textbooks; literature citations (7 to 10) refer to several of these textbooks.

where K = the equilibrium constant;
a_2 = the activity of sodium bisulfite;
a_1 = the activity of sodium sulfite;
a_S = the activity of dissolved sulfur dioxide;
a_w = the activity of water;
γ_2 = the mean ionic molal activity coefficient of sodium bisulfite;
m_2 = the molality of sodium bisulfite;
γ_1 = the mean ionic molal activity coefficient of sodium sulfite;
m_1 = the molality of sodium sulfite.

Mean ionic molal activity coefficients are used primarily in this study and are subsequently called simply "activity coefficients". The only exception to this is in the case of ions, where the symbol γ is used for the ionic activity coefficient. The usual conventions defining the standard states as given by Lewis and Randall (7) are used.

DETERMINATION OF EQUILIBRIUM COMPOSITION

The equilibrium equation, Equation (3), can be considered as an equation with two unknowns, m_1 and m_2, if the other quantities in the equation are known. Another equation with the same two unknowns is the material balance equation for the total sodium in the system; this equation is

$$m_{Na} = 2 m_1 + m_2 \qquad (4)$$

where m_{Na} = molality of total sodium in the system. [Equation (4) neglects the small number of sodium ions in the solution that are not accounted for by the concentrations of sodium sulfite and sodium bi-

sulfite.] Thus, Equations (3) and (4) can be solved simultaneously for the molality of sodium sulfite m_1 and the molality of sodium bisulfite m_2 in the system. Only the concentration of the minor constituents in the system can be estimated since activity-coefficient data for ions are not available. The methods of evaluation used for each of the other quantities in the equilibrium equation are now discussed.

ACTIVITY COEFFICIENTS

The isopiestic vapor-pressure comparison technique was used to obtain data from which the activity coefficients of sodium sulfite in aqueous solution were calculated. This technique was selected because of its simplicity, high accuracy and general applicability. In this method, two solutions are isopiestically compared by being placed in separate dishes in a closed vessel at constant temperature. The solvent is the same in both solutions. Solvent from the solution which has the higher vapor pressure, or more strictly the higher solvent activity, distils into the vapor space above the dishes and condenses into the other solution. At equilibrium, the two solutions have equal solvent activities. The concentrations of the solutions at equilibrium are calculated from the initial concentrations and the mass of solvent gained or lost during the equilibration; these equilibrium concentrations are called "isopiestic concentrations". The data from a series of isopiestic measurements in which the concentrations of the solutions are varied are called "isopiestic data".

If the activity coefficients of the solute in one of the solutions are known, the activity coefficients of the solute in the other solution

can be calculated from the isopiestic data. The solute for which the activity data are known is called the "reference" solute. In these measurements, aqueous sodium sulfite solutions were equilibrated isopiestically with aqueous sodium chloride solutions at 25°C.; the activity-coefficient data for sodium chloride in aqueous solution are well established.

The activity coefficients of sodium sulfite in aqueous solution were calculated from an equation derived from the Gibbs-Duhem equation. Application of the Gibbs-Duhem equation to isopiestic sodium sulfite and sodium chloride solutions yields:

$$\underline{m}_1 \, d \ln \underline{a}_1 + \underline{m}_w \, d \ln \underline{a}_w = 0 \qquad (5)$$

$$\underline{m}_R \, d \ln \underline{a}_R + \underline{m}_w \, d \ln \underline{a}_w = 0 \qquad (6)$$

where the subscript R refers to the reference or, in this case, to the sodium chloride solution. The second term in each of these equations is identical since the activities of water in two isopiestic solutions are equal. Equations (5) and (6) can be combined and integrated to yield:

$$\ln \underline{\gamma}_1 = \ln \underline{\gamma}_R + \ln (2\underline{m}_R/\underline{m}_1) + 2 \int_0^{\underline{a}_{\pm R}} \left(\frac{2\underline{m}_R}{3\underline{m}_1} - 1 \right) \frac{d \sqrt{\underline{a}_{\pm R}}}{\sqrt{\underline{a}_{\pm R}}} \qquad (7)$$

In this equation $\underline{a}_{\pm R}$ equals the mean ionic activity of the sodium chloride reference solution. The last term of the right side of the equation must be evaluated graphically. Since the lower limit of integration is zero activity at infinite dilution, it is necessary

to extrapolate either the isopiestic data or the curve plotted for the graphical integration to zero activity. This extrapolation always involves a certain amount of uncertainty.

The differential form of Equation (7) can be integrated from a finite dilute concentration for which isopiestic measurements were actually made. If this is done, the result is

$$\ln(\gamma_1/\gamma_{1(r)}) = \ln(\gamma_R/\gamma_{R(r)}) + \ln\frac{\underline{m}_R/\underline{m}_1}{(\underline{m}_R/\underline{m}_1)_r} + 2\int_{\underline{a}_{\pm R(r)}}^{\underline{a}_{\pm R}} \left(\frac{2\underline{m}_R}{3\underline{m}_1} - 1\right)\frac{d\sqrt{\underline{a}_{\pm R}}}{\sqrt{\underline{a}_{\pm R}}} \qquad (8)$$

where the second subscript $\underline{r}$ stands for the dilute solution used for the lower limit of integration. This equation then permits the calculation of $\gamma_{\underline{Y}}/\gamma_{1(r)}$, the ratio of the activity coefficient of sodium sulfite at any concentration to the activity coefficient of the sodium sulfite in the dilute solution designated by the subscript r.

The activity coefficients of sodium sulfite at any concentration can be calculated from these ratios if $\gamma_{1(r)}$ can be evaluated. An extended form of the Debye-Hückel equation can be used to calculate $\gamma_{1(r)}$ if it can be accurately fitted to the activity coefficient data calculated from Equation (8). One extended form of the Debye-Hückel equation is

$$\ln\gamma = \frac{-b\sqrt{\underline{I}}}{1 + \underline{A}\sqrt{\underline{I}}} + \underline{B}\,\underline{m} \qquad (9)$$

where $\underline{b}$ = the Debye-Hückel limiting slope--specific for each valence-type of electrolyte;
$\underline{A}$ = a constant which is a function of the effective diameter of the ionic atmosphere;
$\underline{B}$ = an empirical constant related to the salting out effect;
$\underline{I}$ = the total ionic strength defined by

$$\underline{I} = \frac{1}{2}\sum_{i} \underline{m}_i \underline{z}_i^2 \qquad (10)$$

In Equation (10) $\underline{z}_i$ is the valence of the ion, i. Equation (9) has been shown to represent activity-coefficient data up to concentrations of one molal for many electrolytes and even up to two molal for some electrolytes. Equation (9) was fitted to the activity-coefficient data calculated from Equation (8) for values of the molality from 0.4 to 1.0 and shown to represent the activity-coefficient ratios calculated from Equation (8) within the accuracy of the experimental measurements. Therefore, the activity coefficients of sodium sulfite were evaluated from the ratios calculated from Equation (8) and $\gamma_{1(r)}$ calculated from Equation (9).

The activity coefficients of sodium bisulfite in aqueous solution were calculated from the McKay-Perring equation (11) using the modifications suggested by Bonner and Holland (12). The equation that was used is

$$\ln(\underline{I}\gamma_2) = \ln(\underline{I}_R\gamma_R) - 55.51/2 \int_1^{\underline{a}_w} \left\{ -\underline{x}_1 \left(\frac{\partial(1/\underline{I})}{\partial \underline{x}_2} \right)_{\underline{a}_w} + 1/\underline{I} - 1/\underline{I}_R \right\} d \ln \underline{a}_w \qquad (11)$$

where $x_1 = I_1/I$ and $x_2 = I_2/I$; a condition of integration is that x_1 be constant during the integration. This equation as it stands is for the calculation of the activity coefficients of sodium bisulfite in sodium sulfite-bisulfite solutions. However, it can be used for a pure sodium bisulfite solution by setting x_1 equal to zero.

Equation (11) is derived from the Gibbs' free energy equation and is designed to be applied to isopiestic data in a manner similar to Equation (7). However, in this case, the activity of the water in the sodium bisulfite solutions was obtained by direct measurement of the vapor pressures of water above the sodium bisulfite solutions rather than by the isopiestic technique. The isopiestic technique was not used because of the problems caused by the volatility of the dissolved sulfur dioxide in the bisulfite solution, and because the use of the dynamic gas saturation vapor-pressure technique permitted the sulfur dioxide and water vapor pressures to be measured simultaneously.

The vapor-pressure data was then converted to molalities of sodium chloride solutions of corresponding vapor pressures, and the activity coefficients of sodium bisulfite were calculated from Equation (11). In making this calculation, the assumption was made that the presence of constituents other than sodium bisulfite in the sodium bisulfite solutions had no significant effect on the calculated activity coefficients. This assumption is discussed further on page 60.

Equation (11) was used also for the calculation of the activity coefficients of sodium bisulfite in sodium sulfite-bisulfite solutions at various values of x_1 and I. A similar equation can be written that

permits the calculation of the activity-coefficient ratios of sodium sulfite in sodium sulfite-bisulfite solutions:

$$3 \ln(\underline{I}\gamma_1/\underline{I}_{(r)}\gamma_{1(r)}) = 2 \ln(\underline{I}_R\gamma_R/\underline{I}_{R(r)}\ \gamma_{R(r)})$$

$$-55.51\int_{\underline{a}_{w(r)}}^{\underline{a}_w}\left\{3\underline{x}_2\left(\frac{\partial(1/\underline{I})}{\partial \underline{x}_1}\right)_{\underline{a}_w} + 3/\underline{I} - 1/\underline{I}_R\right\} d \ln \underline{a}_w \qquad (12)$$

The activity coefficients of sodium sulfite were calculated from these activity-coefficient ratios and an assumed value of $\gamma_{1(r)}$. It is necessary to use this form of the equation rather than the form used for Equation (11) because the extrapolation required to evaluate the integral could not be performed with sufficient accuracy. The data used for these calculations were the isopiestic data for sodium sulfite solutions, the converted vapor-pressure data for sodium bisulfite solutions, and isopiestic data determined for sodium sulfite-bisulfite solutions where the molal ratio of sulfite to bisulfite was about 1:1. These three sets of data were plotted together, and smooth curves were drawn through the data to permit interpolation of the data for the values of $\underline{x}_1$ used in the equation.

ACTIVITY OF WATER

The activity of water for any given aqueous solution is equal to the ratio of the fugacity of the water vapor above the given solution to the fugacity of pure water at the same temperature. In this case

vapor pressure can be substituted for fugacity within the accuracy of the experimental data. Thus, the data used for the calculation of activity coefficients in sodium sulfite-bisulfite solutions were converted to water vapor-pressure data and used to calculate the activity of water, $\underline{a}_w$.

THE EQUILIBRIUM CONSTANT

The equilibrium constant, $\underline{K}$, can be shown to be the ratio of the first and second ionization constants of sulfurous acid. Thus, $\underline{K}$ was calculated from the values of these ionization constants given in the literature.

ACTIVITY OF SULFUR DIOXIDE

One form of the Henry's law relationship is expressed by Equation (13):

$$\underline{a}_S = \underline{H}\underline{f}_S = \underline{H}\underline{p}_S \qquad (13)$$

where $\underline{a}_S$ = activity of sulfur dioxide in the liquid phase;
$\underline{H}$ = Henry's law constant for sulfur dioxide in water;
$\underline{f}_S$ = fugacity of sulfur dioxide in the vapor phase;
$\underline{p}_S$ = vapor pressure of sulfur dioxide in the vapor phase.

The vapor pressure of sulfur dioxide can be substituted for the fugacity within the accuracy of the experimental data. If a system has been shown to follow Henry's law, the activity of the dissolved gas is equal to the product of the Henry's law constant and the fugacity of the gas in the vapor phase. The system sulfur dioxide-water has been shown to follow Henry's law up to a sulfur dioxide partial pressure of about

1000 mm. of mercury (13). The activity of the dissolved sulfur dioxide then in the sulfur dioxide-water system is given by Henry's law. Since the chemical potential of a component is the same in each phase of a system at equilibrium, the chemical potential of sulfur dioxide in the vapor phase above a sulfur dioxide-water solution must be the same as that in the solution. Thus, if in two different systems the chemical potentials of sulfur dioxide in the vapor phase of each system are equal, the activities of the sulfur dioxide in the liquid phase in each system must also be equal. If two systems have equal vapor pressures of sulfur dioxide in the vapor phase, they also have equal chemical potentials of sulfur dioxide in the vapor phase. Therefore, the activity of dissolved sulfur dioxide in the system sodium sulfite-sodium bisulfite-water can be calculated from the Henry's law constant for the sulfur dioxide-water system and the vapor pressure of sulfur dioxide above the sodium sulfite-sodium bisulfite-system. The vapor pressures of sulfur dioxide above sodium bisulfite solutions were measured; the vapor pressures of sulfur dioxide above sodium sulfite-bisulfite solutions were estimated from the data of Johnstone, et al. (5).

EXPERIMENTAL PROCEDURES

ISOPIESTIC MEASUREMENTS OF SODIUM SULFITE SOLUTIONS

The apparatus and procedure used for the isopiestic measurements on sodium sulfite solutions were essentially the same as those used by Sinclair (14) and Robinson and Sinclair (15). The closed vessel used for the equilibration of the sodium sulfite and sodium chloride solutions was a vacuum desiccator. The solutions were weighed into small dishes, and the dishes were placed on a disk mounted inside the desiccator. The dishes were made of fine silver and the disk of high conductivity copper to insure that the dishes would be in thermal equilibrium with each other. To speed the equilibration, the desiccator was evacuated to a pressure of about 20 mm. of mercury before being placed in the constant temperature bath. The desiccator was placed in the constant temperature bath at 25±0.005°C. for one to several days--a longer time of equilibration being required for the more dilute solutions. The desiccator was rocked in the bath to insure good mixing of the solutions. The final or isopiestic concentration of each solution was calculated from the concentration and weight of the solution added to each dish initially, and the weight of solution in each dish after equilibration. The concentration of the solutions was varied so that the isopiestic data included concentrations from 0.2 to 2.2 molal.

The sodium chloride reference solutions were prepared from Baker's reagent-grade sodium chloride and conductivity water. A sodium chloride solution having a concentration of about 6 molal was prepared gravimetrically as a stock solution. A stock sodium sulfite solution having

a concentration of about 2 molal was prepared gravimetrically by adding the stoichiometric amount of sulfur dioxide to a concentrated sodium hydroxide solution so that the ratio of total sulfur dioxide to total sodium in the solution was exactly 0.5. The sodium hydroxide solution used was prepared from Baker's reagent-grade 50% sodium hydroxide solution. The sulfur dioxide used was Ansul's refrigeration grade; the manufacturer's assay was 99.98% SO_2.

During the preparation and handling of these solutions, care was taken to keep oxygen exposure to a very minimum since sulfite solutions are readily oxidized by exposure to air. The preparation of the sodium sulfite solutions, and the various steps in the isopiestic procedure involving exposure of the solutions were carried out in a nitrogen chamber where the oxygen level was maintained below 2000 p.p.m. A detailed description of the apparatus and procedures is given in Appendix I together with sample calculations.

ISOPIESTIC MEASUREMENTS ON SODIUM SULFITE-BISULFITE SOLUTIONS

The same procedure and apparatus were used to obtain isopiestic measurements on sodium sulfite-bisulfite solutions as were used for the sodium sulfite solutions. The sodium sulfite-bisulfite solutions used had a molal ratio of sulfite to bisulfite equal to approximately one.

VAPOR-PRESSURE MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

An apparatus was designed and a procedure developed to measure the vapor pressures of both water and sulfur dioxide above aqueous sodium

bisulfite solutions. The apparatus was essentially a combination of those used by Johnstone (16) and Taylor (2). The procedure was essentially that of Johnstone with modifications to permit reproducibility of the data to about 0.5%.

The apparatus was constructed so that dry nitrogen was passed through successive portions of the sodium bisulfite solution in such a manner that the vapor phase was in equilibrium with the liquid phase before the nitrogen stream left the last portion of the bisulfite solution. The equilibrium amounts of sulfur dioxide and water vapor that were picked up from the bisulfite solution were quantitatively removed from the nitrogen after it left the last portion of the bisulfite solution and the nitrogen was collected. The masses of the collected nitrogen, and of the sulfur dioxide and water vapor removed from the nitrogen were measured. These data together with the total pressure and temperature were used to calculate the vapor pressures of sulfur dioxide and water above the sodium bisulfite solution. The vapor-pressure data were obtained for sodium bisulfite solutions from 0.5 to 7.0 molality of total sodium. The sodium bisulfite solutions were prepared in the same manner as the sodium sulfite solutions.

A detailed description of the apparatus used and the procedure followed are given in Appendix II. A sample calculation is also given.

pH MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

The pH of sodium bisulfite solutions was measured as a function of concentration using a Beckman Model H-2 glass electrode pH meter. The

measurements were made in the usual manner with the temperature controlled at 25.0±0.1°C. The detailed procedure is given in Appendix III.

PRESENTATION AND ANALYSIS OF EXPERIMENTAL RESULTS

ISOPIESTIC MEASUREMENTS ON SODIUM SULFITE SOLUTIONS

Sodium sulfite solutions were equilibrated isopiestically with sodium chloride solutions at 25°C. The activity data for sodium chloride were taken from page 461 of Robinson and Stokes (9). The results are shown in Table I. The last column in the table gives the "isopiestic ratios" of sodium sulfite and sodium chloride. The isopiestic ratio is defined as the product of the number of ions produced by the dissociation of one molecule of the reference electrolyte and the molality of that electrolyte divided by the product of the number of ions produced by the dissociation of one molecule of the other electrolyte and the molality of that electrolyte. This quantity is used in plotting the isopiestic data since it has a value of unity at infinite dilution. The isopiestic data are presented graphically in Fig. 1; the isopiestic ratio has been plotted against the molality of sodium sulfite. With the exception of Run 42, all of the values in Table I are the mean of three individual determinations. That is, the solutions in six dishes, three containing sodium sulfite solution and three containing sodium chloride solution, were equilibrated at the same time. The data for Run 42 are based on two determinations. The number in parenthesis after each value in the table is the standard error of the mean value expressed as a percentage of the mean value.

The reproducibility of the data was demonstrated for both the sodium chloride and sodium sulfite solutions. In some of the preliminary

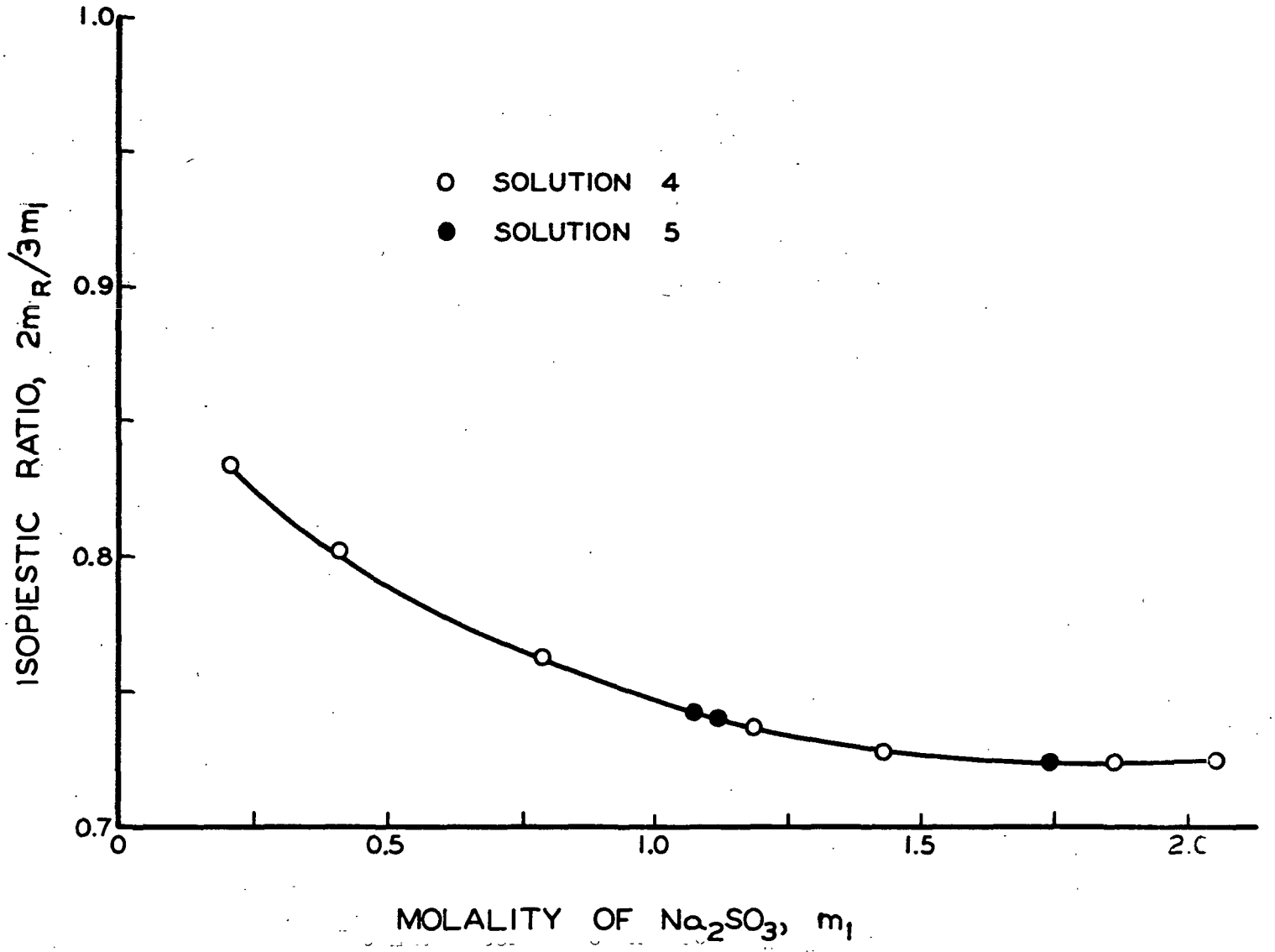

Figure 1. Isopiestic Data for Na_2SO_3 at 25°C.

TABLE I

MOLALITIES OF ISOPIESTIC Na_2SO_3 AND NaCl SOLUTIONS AT 25°C.

Run	Solution No.	Molality of NaCl, m_R	Molality of Na_2SO_3, m_1	Isopiestic Ratio, $2m_R/3m_1$
48	4[a]	0.2595 (0.11%)[b]	0.2071 (0.06%)	0.8354 (0.12%)
36	4	0.4920 (0.16%)	0.4095 (0.08%)	0.8010 (0.18%)
34	4	0.8982 (0.04%)	0.7844 (0.05%)	0.7633 (0.07%)
38	4	1.304 (0.06%)	1.178 (0.01%)	0.7381 (0.06%)
43	4	1.571 (0.06%)	1.436 (0.07%)	0.7294 (0.10%)
42	4	2.028 (0.02%)	1.865 (0.05%)	0.7251 (0.05%)
45	4	2.239 (0.07%)	2.058 (0.07%)	0.7252 (0.10%)
40	5	1.195 (0.02%)	1.073 (0.04%)	0.7425 (0.05%)
39	5	1.233 (0.09%)	1.110 (0.08%)	0.7409 (0.12%)
47	5	1.892 (0.07%)	1.742 (0.09%)	0.7240 (0.12%)

[a] These numbers refer to the various stock sodium sulfite solutions.

[b] The number in parenthesis after each value is the standard error of the value expressed as a percentage of the value.

runs two different stock solutions of sodium chloride were used with the same stock sodium sulfite solution. No significant difference was observed when the results using different sodium chloride solutions were compared. Using different stock sodium sulfite solutions with the same stock sodium chloride solution failed to give results that were reproducible within the desired limits. When the isopiestic concentrations were greater than 0.5 molal, a run was rejected on the basis of failure to reach equilibrium in the allotted time if the standard deviation of the isopiestic concentration of one of the solutions was greater than 0.1%. It was necessary to accept slightly greater standard deviations when the concentrations were below 0.5 molal because of the magnification of errors at these low concentrations.

Therefore, isopiestic data from runs made with the same stock sodium chloride solution could be expected to agree with each other within 0.1% most of the time if the concentrations are greater than 0.5 molal. However, the results using stock sodium sulfite solution 3 were consistently higher than the results obtained using stock sodium sulfite solutions 4 and 5. Since the least accurate step in the stock sulfite solution preparation procedure is the volumetric determination of the concentration of the starting sodium hydroxide solution, the volumetric determination was replaced with a gravimetric sodium determination. (A detailed description of this procedural modification is given in Appendix I.) The results of the gravimetric sodium determination showed that the results of the volumetric determinations were incorrect. The sulfur dioxide to sodium ratio of stock sulfite solutions 4 and 5 was then readjusted on the basis of the gravimetric sodium determinations, and these readjusted solutions were used for the runs listed in Table I. The reproducibility of the results using sulfite solutions 4 and 5 was better than 0.1% for the runs with concentrations above 0.5 molal.

The small amount of impurities present in the sodium chloride and sodium sulfite solutions had no significant effect on the isopiestic data. The stock sodium chloride solution was compared isopiestically with a potassium chloride solution prepared from Baker's reagent-grade potassium chloride. The results of this comparison agreed with data in the literature to better than 0.01%. The carbonate contamination of the sulfite solutions was minimized by starting with a 50% sodium hydroxide solution containing 0.02% carbonate and by using deaerated water exposed

only to nitrogen after deaeration. The effect of the presence of up to 2000 p.p.m. oxygen in the nitrogen chamber was shown to be negligible. One particular run was exposed to the chamber atmosphere for periods of time sufficient to allow for about 80 times more oxygen diffusion into the solution than would occur during the normal procedure. The results of this run were within 0.1% of the curve drawn through the other data points. A reddish-brown precipitate resembling ferric hydroxide settled out of the stock sodium sulfite solutions. Spectrographic analysis showed that the precipitate was mostly iron. Since the precipitate settled out of solution and amounted to only 0.0008% of the total mass of solution, it was concluded that the presence of this precipitate in the stock sulfite solutions had no significant effect on the isopiestic data.

It is believed that the isopiestic data as represented by the curve of Fig. 1 have a standard error of about 0.1%.

ISOPIESTIC MEASUREMENTS ON SODIUM SULFITE-BISULFITE SOLUTIONS

Sodium sulfite-bisulfite solutions having a molal ratio of sulfite to bisulfite of about one were equilibrated isopiestically with sodium chloride solutions at 25°C. The results are given in Table II and Fig. 2; Table II is arranged similarly to Table I.

The comments on reproducibility and purity given in the preceding section concerning sodium sulfite solutions apply equally to these solutions. Thus, it is believed that the isopiestic data as represented by the curve of Fig. 2 have a standard error of about 0.1%.

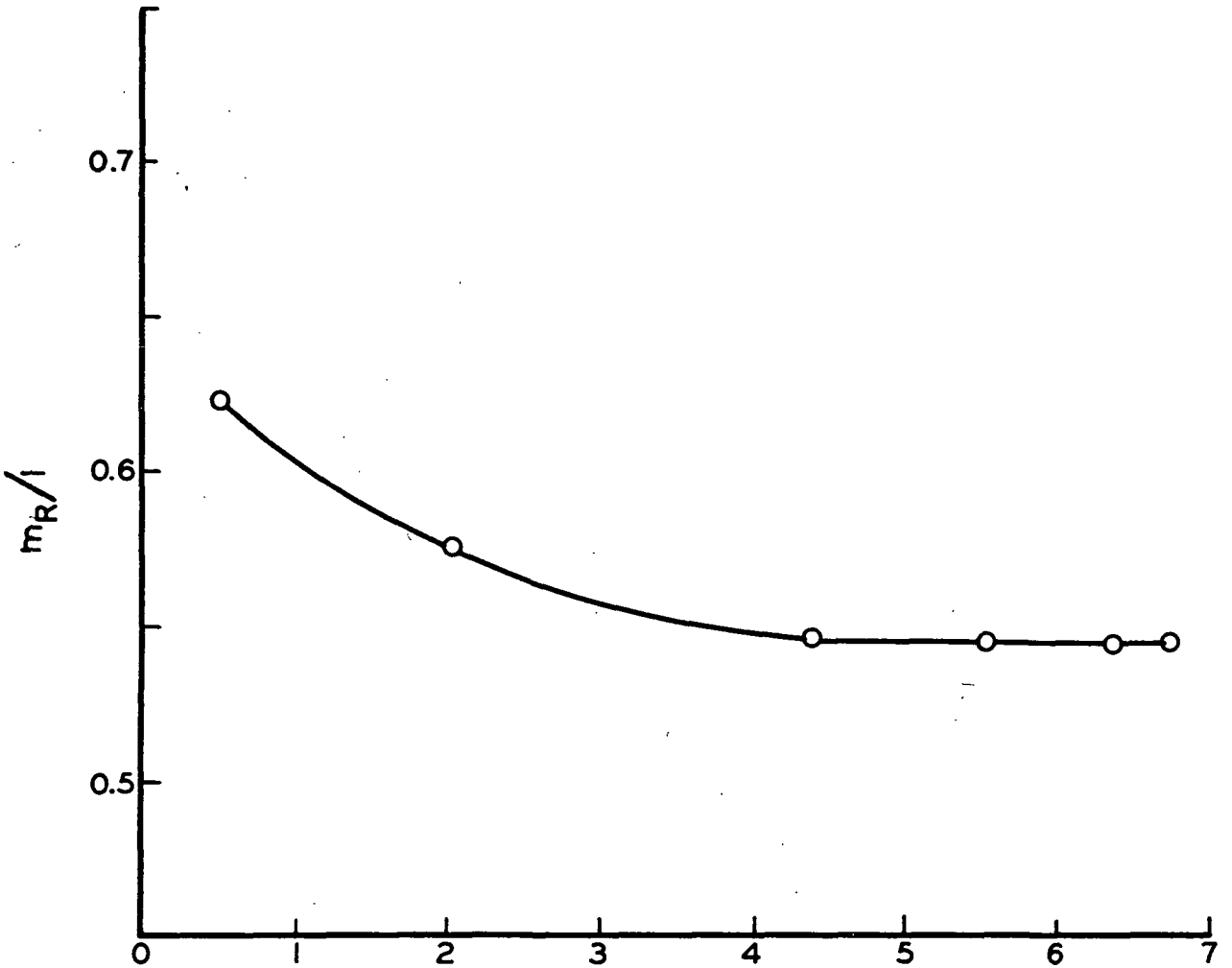

Figure 2. Isopiestic Data for Na_2SO_3-$NaHSO_3$ Solutions at 25°C.

TABLE II

MOLALITIES OF ISOPIESTIC Na_2SO_3-$NaHSO_3$ AND NaCl SOLUTIONS AT 25°C.

Run	Molality of NaCl, m_R	Total Ionic Strength of Na_2SO_3-$NaHSO_3$ Solutions, I	m_R/I
31	0.2962 (0.14%)[a]	0.4764 (0.09%)	0.6217 (0.16%)
35	1.150 (0.03%)	2.001 (0.01%)	0.5746 (0.03%)
28	2.384 (0.03%)	4.364 (0.02%)	0.5464 (0.04%)
37	2.993 (0.06%)	5.490 (0.08%)	0.5451 (0.10%)
30	3.462 (0.03%)	6.327 (0.08%)	0.5471 (0.08%)
26	3.679 (0.01%)	6.709 (0.03%)	0.5483 (0.03%)

[a] The number in parenthesis after each value is the standard error of the value expressed as a percentage of the value.

VAPOR-PRESSURE MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

The vapor pressures of sulfur dioxide and water above sodium bisulfite solutions were measured as a function of the total sodium molality, m_{Na}, at 25°C. The results are given in Table III. With the exception of the data when m_{Na} is equal to 7, the values given in the table are the mean of five determinations; the values when m_{Na} is equal to 7 are the mean of four determinations. The standard errors of the means are less than 0.5% in every case except two; in these two cases the absolute values of the standard error are about the same as they are for the other concentrations.

These data have been plotted in Fig. 3. Straight lines have been drawn through the data points in both cases. For the water vapor-pressure data, the line shown is the regression line calculated from the data with the restriction that the line intersect the ordinate at

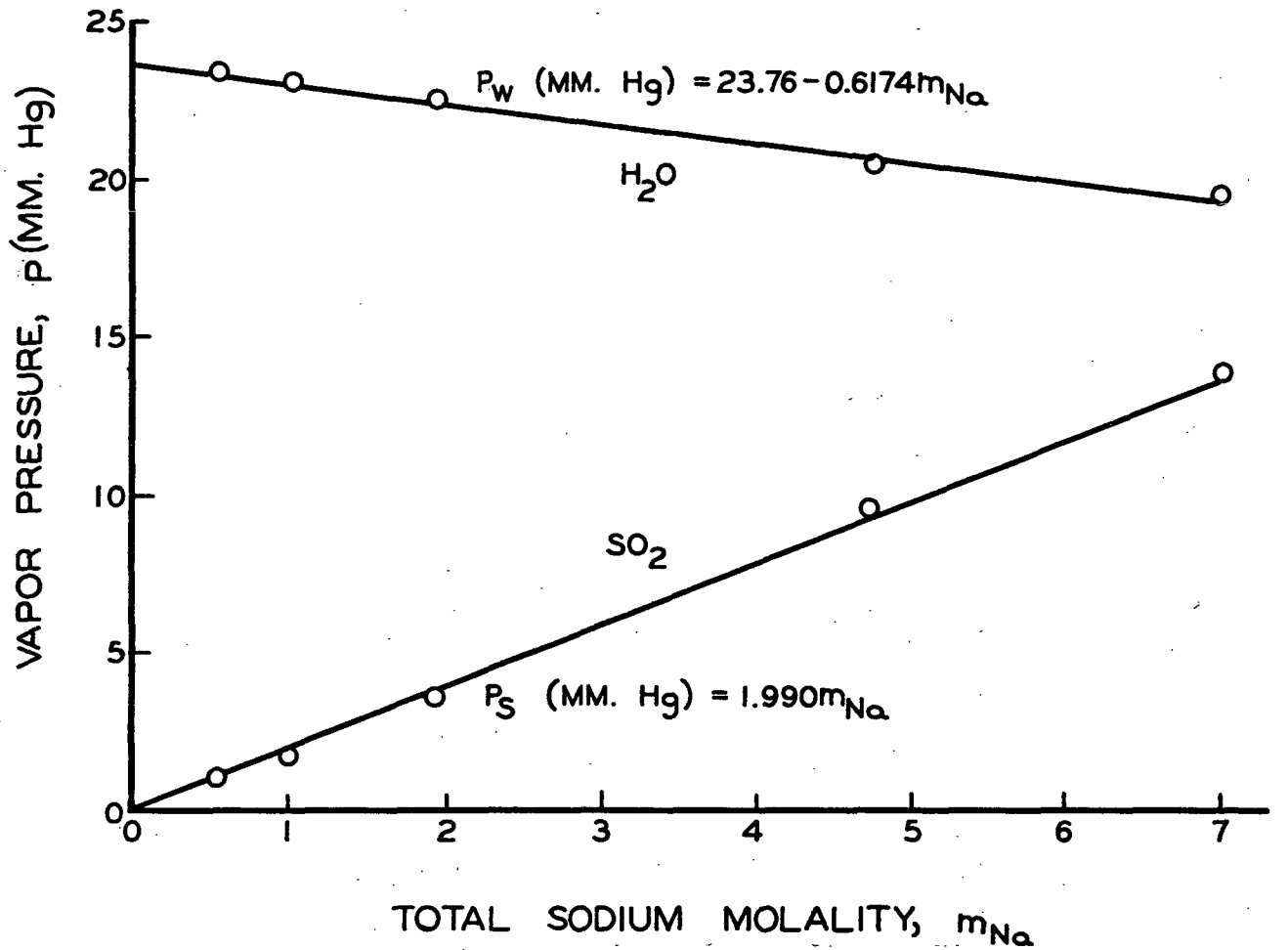

Figure 3. Vapor Pressures of H_2O and SO_2 above $NaHSO_3$ Solutions at 25°C.

TABLE III

VAPOR PRESSURES OF H_2O AND SO_2 ABOVE $NaHSO_3$ SOLUTIONS AT 25°C.

Total Sodium Molality, m_{Na}	H_2O Vapor Press., mm. Hg		SO_2 Vapor Press., mm. Hg	
0	23.76	--	--	--
0.5723	23.38	(0.4%)[a]	1.01	(2.0%)
1.048	23.08	(0.3%)	1.80	(1.0%)
1.943	22.57	(0.2%)	3.64	(0.2%)
4.745	20.65	(0.3%)	9.59	(0.2%)
7.015	19.57	(0.4%)	13.98	(0.1%)

[a] The number in parenthesis after each value is the standard error of the value expressed as a percentage of the value.

a value equal to the vapor pressure of pure water at 25°C. This line was not significantly different from the regression line calculated without the restriction. Standard statistical calculations showed that the standard error of a value of the vapor pressure calculated from the regression line is about the same as the standard error of each of the values given in Table III. A linear regression line was also calculated for the sulfur dioxide vapor-pressure data. A comparison of the data points calculated from this regression line with the measured data points shows that, with the exception of the data point when m_{Na} equals 7, the calculated value deviates from the measured value by an amount equal to about eight times the standard deviation. Nevertheless the fitting of a curvilinear regression line with an inflection point did not seem justifiable on the basis of the precision of the data alone. The significance of the accuracy of the sulfur dioxide vapor-pressure data is discussed further in regard to the equilibrium calculations in the calculation section of the thesis.

The stock sodium bisulfite solution used for the vapor-pressure determinations was prepared in the same manner as the sulfite and sulfite-bisulfite solutions. Therefore, the previous discussion regarding the reproducibility and purity of these solutions applies equally to the sodium bisulfite solutions. It was not possible to prevent some contact of these solutions with air during the process of preparing the apparatus for the vapor-pressure determinations. Johnstone, et al. (5) have shown that the addition of 0.1% of hydroquinone to sodium sulfite-bisulfite solutions inhibits oxidation. Therefore, 0.1% of hydroquinone was added to the stock solution during its preparation.

In view of the precision of each data point and the possible sources of error, it is believed that the water vapor-pressure data as represented by the calculated regression line have a standard error of about 0.8%; the standard error of the regression line representing the sulfur dioxide vapor-pressure data is believed to be 0.2-0.3 mm. of mercury or about 5% over most of the range of the data. The vapor pressures of sulfur dioxide above sodium bisulfite solutions obtained in this study are six to seven times lower than the corresponding data reported by Kotzerke (6). In the course of attempting to reconcile this difference, discrepancies were found in the calculation procedure used by Kotzerke. Recalculation of Kotzerke's data (17) yielded values for the vapor pressure of sulfur dioxide which are the same order of magnitude as the data obtained in this study. Further verification of the vapor-pressure data of this study was obtained by measuring the approximate value of the total vapor pressure above sodium bisulfite

solutions using a Van Slyke apparatus (18), and by extrapolating Johnstone's sulfur dioxide vapor-pressure data for sodium sulfite-bisulfite mixtures (5); these results corroborated the order of magnitude of the vapor-pressure data obtained in this study.

pH MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

The pH of sodium bisulfite solutions was measured as a function of concentration at 25.0±0.1°C. The measurements were made on solutions prepared from a portion of the stock sodium bisulfite solution used for the vapor-pressure measurements. The results are given in Table IV and in Fig. 4.

TABLE IV

pH OF $NaHSO_3$ SOLUTIONS

Total Sodium Molality, m_{Na}	pH
0.0618	4.51
0.1145	4.41
0.1508	4.34
0.2225	4.33
0.3074	4.23
0.3838	4.20
0.4586	4.20
0.4928	4.20
0.5495	4.19
0.6237	4.16
0.7282	4.13
0.9817	4.09
1.398	4.01
1.931	3.92
2.750	3.82
3.628	3.78
4.177	3.73
5.078	3.70
5.970	3.70
7.015	3.70

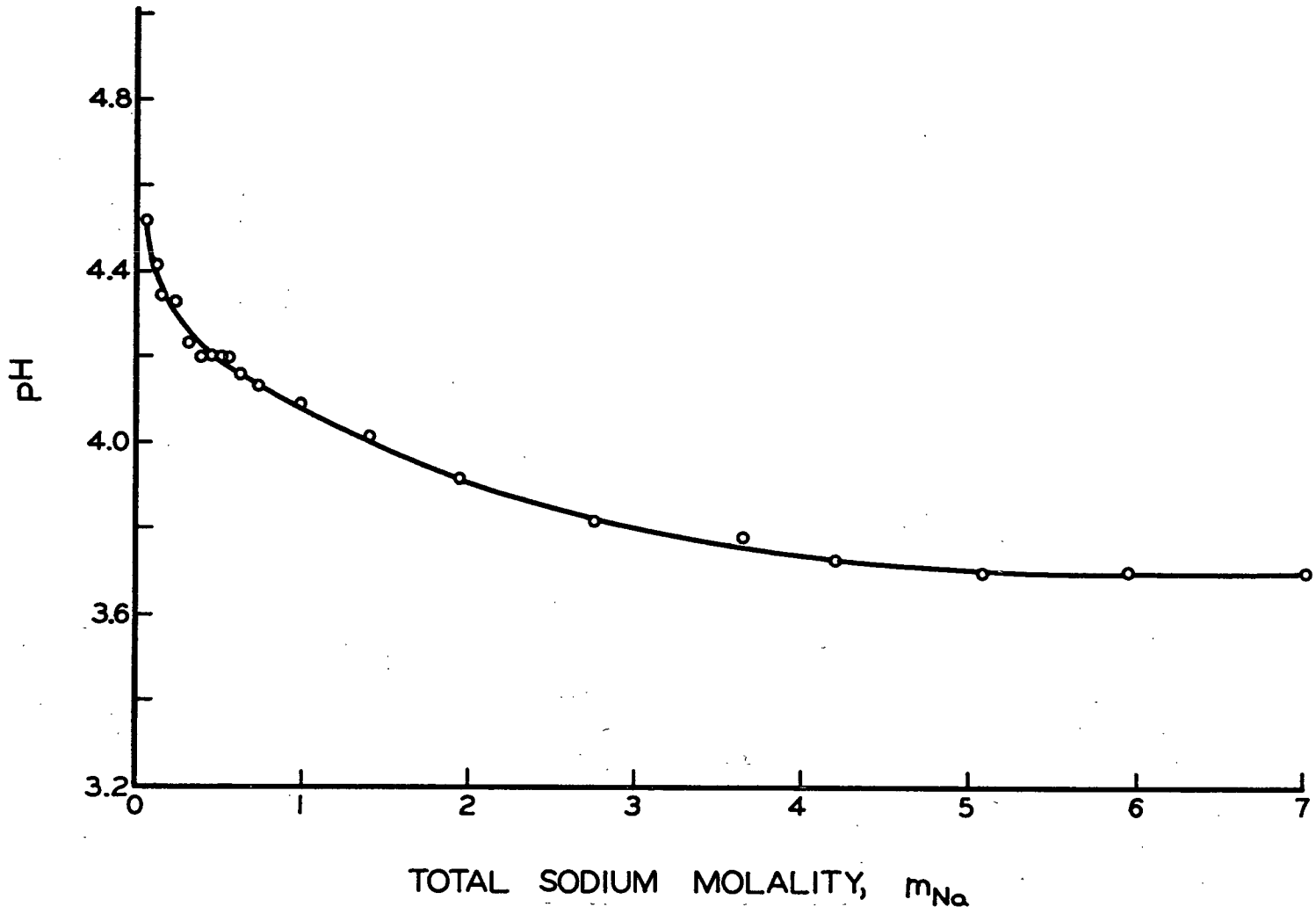

Figure 4. pH of $NaHSO_3$ Solutions at 25°C.

The usual accuracy of pH measurements using a glass electrode is a few hundredths of a pH unit. In the case of measuring the pH of sodium bisulfite solutions, two additional factors affect the accuracy of the pH measurements: oxidation and volatilization of sulfur dioxide. In making the pH measurements reported here it was observed that there was no significant difference in the pH values if the time from the dilution of the stock solution to the pH measurement was varied from a few hours to 24 hours. Also, there was no measureable change in the pH during the time the solution was exposed to air when the pH was being measured even when a period of five minutes had elapsed. Thus, the effects of oxidation and loss of sulfur dioxide should be negligible in these measurements. Therefore, it is believed that the pH data as represented by the curve of Fig. 4 are accurate to within a few hundredths of a pH unit.

The pH of sodium bisulfite solutions has been reported in the literature (19), (20). These pH determinations were made in connection with pulping studies and were made only on dilute solutions. The shape of the smooth curves drawn through the pH data from each of the pulping studies is similar; but there is a difference in magnitude from 0.4 to 0.9 pH units. One worker considers this order of agreement a check on the other worker's measurements. The pH data of this study do not differ from either of the other workers' data by more than 0.7 pH units. It is believed that the pH data obtained in this study are more accurate.

EQUILIBRIUM COMPOSITION OF THE SYSTEM SODIUM SULFITE-SODIUM BISULFITE-WATER

The data obtained in the experimental program of this thesis together with certain data available in the literature were used to determine the equilibrium composition of the system sodium sulfite-sodium bisulfite-water. The terms in the equilibrium equation, Equation (3), were evaluated in the manner previously discussed. Then the equilibrium compositions of the various solutions were determined.

CALCULATION OF ACTIVITY COEFFICIENTS

ACTIVITY COEFFICIENTS OF SODIUM SULFITE

The activity coefficients of sodium sulfite in aqueous solution were calculated from the isopiestic data obtained in this study. The activity coefficients were calculated from the activity-coefficient ratios and the value of $\gamma_{1(r)}$. The activity-coefficient ratios were calculated from Equation (8) and the value of $\gamma_{1(r)}$ was calculated from the fitted Debye-Hückel equation, Equation (9). The final activity-coefficient data for sodium sulfite are given in Table V. The activity coefficients shown in parentheses were calculated from the fitted Debye-Hückel equation. The details of the analysis of the isopiestic data, the calculation of the activity-coefficient ratios, the fitting of the Debye-Hückel equation, and the calculation of the final values of the activity coefficients are given in Appendix IV; a sample calculation is also given there.

TABLE V

ACTIVITY COEFFICIENTS OF Na_2SO_3 AT 25°C.

Molality	Activity Coefficients
0.0333	(0.5710)[a]
0.0667	(0.4863)
0.1	(0.4378)
0.2	(0.3600)
0.3	(0.3189)
0.4	(0.2920)
0.5	0.2724
0.6	0.2572
0.7	0.2448
0.8	0.2345
0.9	0.2257
1.0	0.2179
1.2	0.2055
1.4	0.1962
1.6	0.1895
1.8	0.1844
2.0	0.1806

[a] Values in parentheses were calculated from the fitted Debye-Hückel equation.

The activity-coefficient data for sodium sulfite have been plotted in Fig. 5 together with similar data for several other 1:2 electrolytes. The absence of significant amounts of foreign substances in the sodium sulfite solutions has already been discussed. It is shown in Appendix IV that the fraction of sodium sulfite that is hydrolyzed in a 0.4 molal sodium sulfite solution is about 0.02%, and that the fraction hydrolyzed decreases with increasing concentration. Therefore, the presence of the products of hydrolysis should have no significant effect on the values of the activity coefficients of sodium sulfite. The

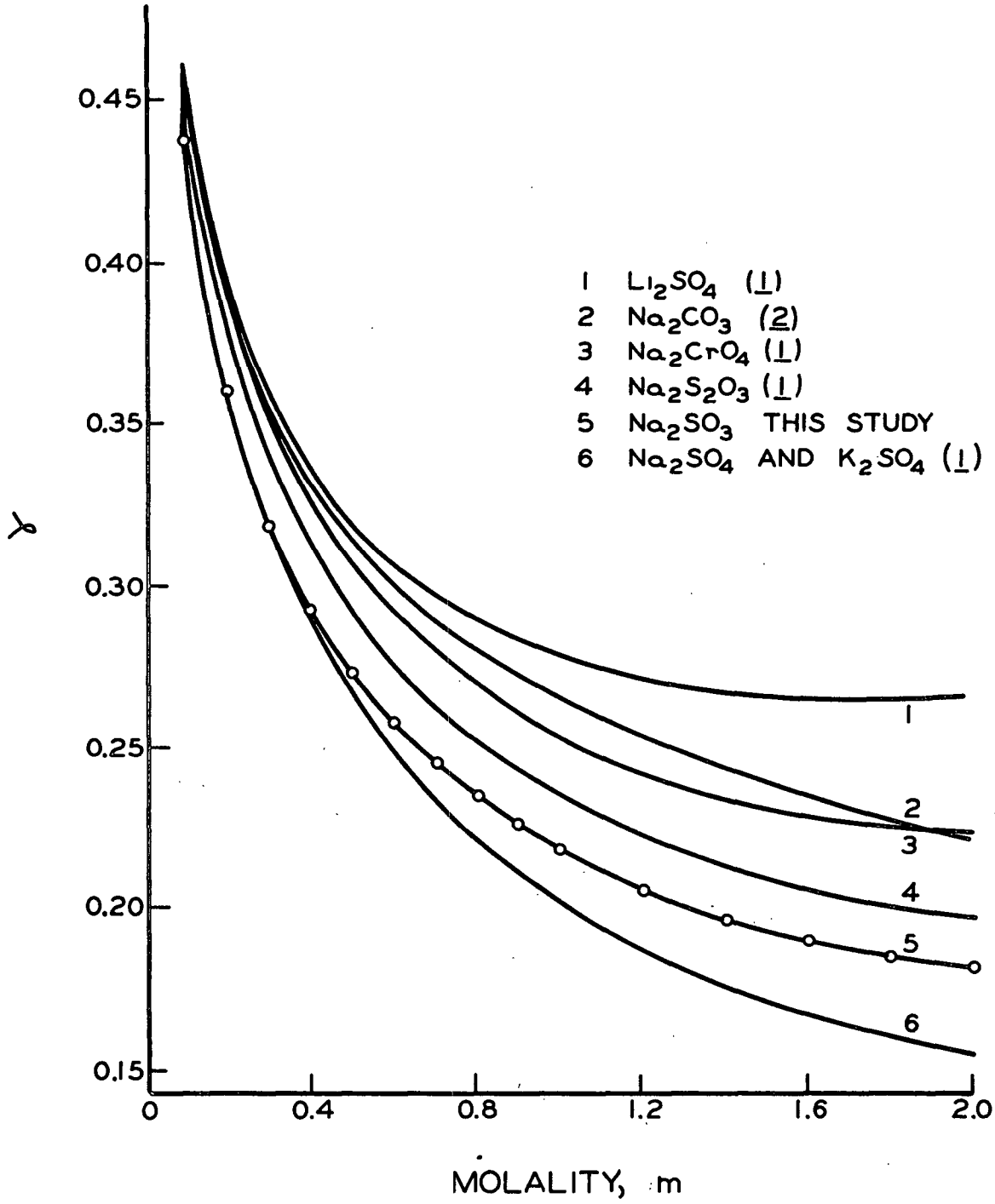

Figure 5. Activity Coefficients of 1:2 Electrolytes at 25°C.

calculated activity-coefficient ratios are estimated to have a standard deviation of about 0.2%. There is no way to determine the accuracy with which the Debye-Hückel equation represents the activity-coefficient data at concentrations below the concentrations for which experimental data have been reliably measured. However, past success in using the Debye-Hückel equation and the closeness of fit in this application indicate that the standard error of the activity-coefficient data should not exceed 0.5%.

ACTIVITY COEFFICIENTS OF SODIUM BISULFITE

The activity coefficients of sodium bisulfite in aqueous solution were calculated from the water vapor-pressure data obtained in this study. A form of the McKay-Perring equation, Equation (11), was used in the manner previously described. The integral in the equation was evaluated graphically--the extrapolation from the last data point to zero being quite certain. This calculation procedure yielded activity-coefficient data for sodium bisulfite solutions for values of the total sodium molality, m_{Na}, from 0.4 to 7. Data were not obtained for values of m_{Na} below 0.4 because of the uncertainty resulting from small errors in the vapor-pressure data, etc. as was described in the case of sodium sulfite in Appendix IV. A curve drawn through the actual vapor-pressure data points was used to evaluate the vapor pressure of water for values of m_{Na} below 2 instead of the calculated regression line.

The activity coefficients for m_{Na} below 0.4 were obtained by extrapolation. The activity-coefficient data for m_{Na} equal to 0.4 to 7 were

plotted against m_{Na}; the curve through the data points was extrapolated to infinite dilution with the aid of the Debye-Hückel limiting slope and an extended form of the Debye-Hückel equation fitted to similar data. The activity-coefficient data for sodium bisulfite solutions are given in Table VI; the data have been plotted together with similar data for 1:1 electrolytes in Fig. 6. If there were no dissociation of sodium bisulfite according to Equation (2), the molality of sodium bisulfite would equal m_{Na}. It was assumed that the molality of sodium bisulfite is equal to m_{Na} in order to compare the activity-coefficient data of sodium bisulfite with that of other 1:1 electrolytes; it is shown subsequently that the error introduced by making this assumption is well within the standard deviation of the activity-coefficient data.

TABLE VI

ACTIVITY COEFFICIENTS OF $NaHSO_3$ AT 25°C.

Molality[a] $NaHSO_3$	Activity Coefficients
0.1	0.705
0.2	0.607
0.3	0.542
0.4	0.492
0.5	0.464
0.65	0.434
0.8	0.410
1.0	0.386
2.0	0.321
3.0	0.292
4.0	0.275
5.0	0.264
6.0	0.257

[a] It was assumed that the molality of sodium bisulfite is equal to the total sodium molality, m_{Na}.

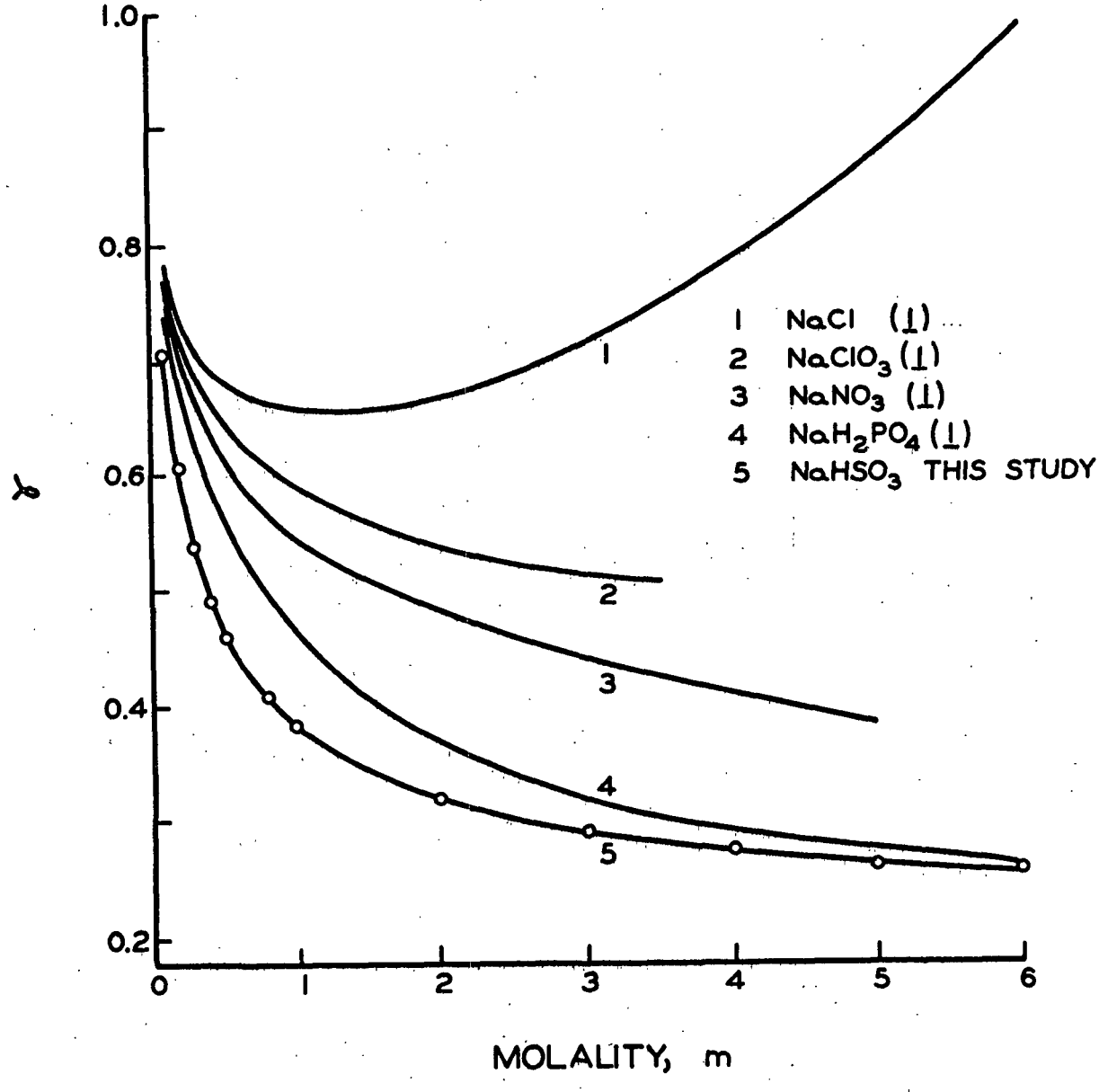

Figure 6. Activity Coefficients of 1:1 Electrolytes at 25°C.

The water vapor-pressure data for sodium bisulfite solutions were estimated to have a standard error of 0.8%. The least accurate step in the calculation procedure for the activity coefficients is the extrapolation step. On the basis of the estimated possible error in extrapolation and the effect of this error on the over-all calculation, a 5% error in the area under the extrapolated portion of the curve would result in about a 1% change in the value of the activity coefficient at $\underline{m}_{Na}$ equal to 0.4 and a progressively smaller change in the value of the activity coefficient as $\underline{m}_{Na}$ increases. However, if the line representing the vapor-pressure data were too low at $\underline{m}_{Na}$ equal to 7 by 0.8%, the standard error, the activity coefficient at $\underline{m}_{Na}$ equal to 3 would be decreased by about 8%. Therefore, it is estimated that the standard error of the activity-coefficient data for sodium bisulfite solutions is about 8%.

ACTIVITY COEFFICIENTS IN SODIUM SULFITE-BISULFITE SOLUTIONS

The activity coefficients of sodium sulfite and sodium bisulfite in sodium sulfite-bisulfite solutions were calculated as a function of the total sulfur dioxide to total sodium ratio and the total ionic strength. The data used for the calculations were the isopiestic data for the sodium sulfite solutions and the sodium sulfite-bisulfite solutions, and the converted water vapor-pressure data for the sodium bisulfite solutions. These data were plotted together and the three sets of data joined with smooth curves. The accuracy with which these curves could be drawn was about the same as the accuracy of the least accurate of the three initial sets of data, the bisulfite data. This plot was

then used to obtain the data required to solve Equations (11) and (12). The activity coefficients of sodium sulfite in the sulfite-bisulfite solutions were calculated from Equation (12). The restriction on the integration of Equation (12) requires that it be evaluated for each value of total ionic strength while the total sulfur dioxide to total sodium ratio is held constant.

The activity coefficient of sodium sulfite at an ionic strength of 0.5, the concentration designated by r in Equation (12), was evaluated by assuming that the activity coefficient of sodium sulfite in all of the sulfite-bisulfite solutions is equal to the activity coefficient of sodium sulfite in water at the same total ionic strength. The activity coefficients for sodium sulfite in all the sulfite-bisulfite solutions were then calculated from this assumed value and the activity-coefficient ratios calculated from Equation (12). These data are given in Table VII and Fig. 7. The values of the activity coefficients of sodium sulfite when the ratio of total sulfur dioxide to total sodium is 1.0 were obtained by extrapolation of the other activity-coefficient data for sodium sulfite.

The activity coefficients of sodium bisulfite in the various sulfite-bisulfite solutions were calculated from Equation (11). The probable error in the extrapolation step in the graphical evaluation of the integral in Equation (11) was within the accuracy of the experimental data. The calculations using Equation (11) yielded activity coefficients for total ionic strengths of 0.65 and higher. These data were plotted together with the activity-coefficient data for pure sodium

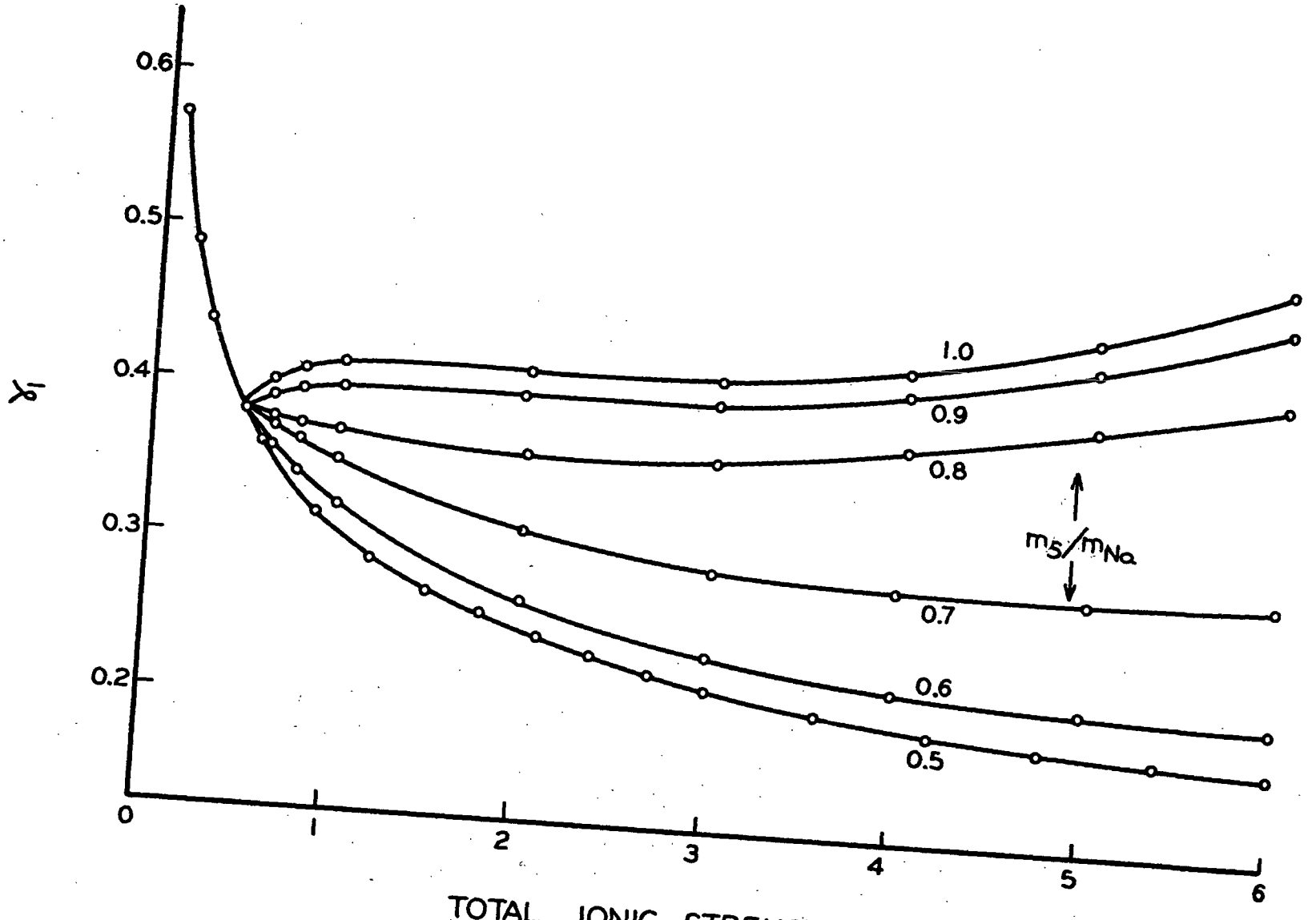

Figure 7. Activity Coefficients of Na_2SO_3 in Na_2SO_3-$NaHSO_3$ Solutions at 25°C.

TABLE VII

ACTIVITY COEFFICIENTS OF SODIUM SULFITE IN SODIUM SULFITE-BISULFITE SOLUTIONS AT 25°C.

Total Ionic Strength, μ	Total Moles Sulfur Dioxide/Total Moles Sodium					
	0.5	0.6	0.7	0.8	0.9	1.0
0.1	0.571	0.571	0.571	0.571	0.571	0.571
0.2	0.486	0.486	0.486	0.486	0.486	0.486
0.3	0.438	0.438	0.438	0.438	0.438	0.438
0.4	0.404	0.404	0.404	0.404	0.404	0.404
0.5	0.379	0.379	0.379	0.379	0.379	0.379
0.65	0.352	0.358	0.372	0.376	0.391	0.402
0.8	0.331	0.345	0.364	0.374	0.395	0.409
1.0	0.308	0.324	0.353	0.372	0.400	0.419
2.0	0.248	0.267	0.314	0.364	0.399	0.420
3.0	0.218	0.238	0.295	0.366	0.401	0.420
4.0	0.199	0.223	0.287	0.379	0.414	0.432
5.0	0.188	0.217	0.288	0.400	0.438	0.460
6.0	0.181	0.216	0.294	0.423	0.473	0.490

bisulfite solutions. Then the activity-coefficient data for the mixtures were extrapolated to infinite dilution by comparison with the activity-coefficient data for sodium bisulfite solutions and by keeping in mind the fact that all of the data curves should approach each other as the total ionic strength approaches zero. These data are given in Table VIII and Fig. 8. The values of the activity coefficients of sodium bisulfite when the ratio of total sulfur dioxide to total sodium is 0.5 were obtained by extrapolation of the other activity-coefficient data for sodium bisulfite.

The accuracy of the calculated activity-coefficient data for sodium sulfite and sodium bisulfite in sodium sulfite-bisulfite solutions is limited by the relatively low accuracy of the converted water-vapor-

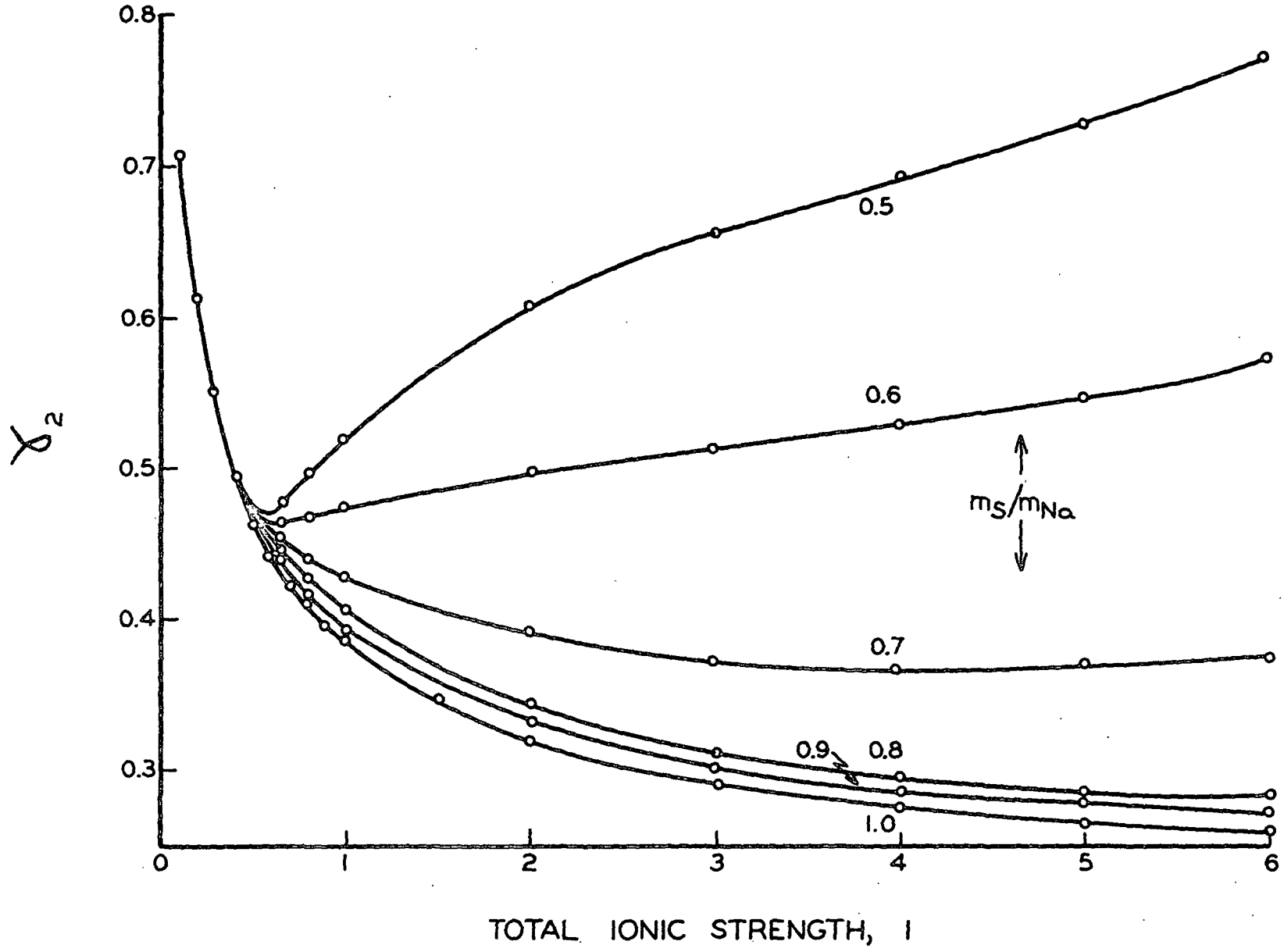

Figure 8. Activity Coefficients of $NaHSO_3$ in Na_2SO_3-$NaHSO_3$ Solutions at 25°C.

TABLE VIII

ACTIVITY COEFFICIENTS OF SODIUM BISULFITE IN SODIUM SULFITE-BISULFITE SOLUTIONS AT 25°C.

Total Ionic Strength, μ	Total Moles Sulfur Dioxide/Total Moles Sodium					
	0.5	0.6	0.7	0.8	0.9	1.0
0.1	0.705	0.705	0.705	0.705	0.705	0.705
0.2	0.613	0.613	0.613	0.613	0.613	0.607
0.3	0.550	0.550	0.550	0.550	0.550	0.542
0.4	0.505	0.505	0.505	0.505	0.505	0.492
0.5	0.475	0.475	0.475	0.475	0.474	0.464
0.65	0.476	0.464	0.451	0.446	0.440	0.434
0.8	0.497	0.469	0.441	0.427	0.416	0.410
1.0	0.517	0.473	0.429	0.406	0.394	0.386
2.0	0.606	0.500	0.393	0.343	0.330	0.321
3.0	0.657	0.516	0.374	0.311	0.301	0.292
4.0	0.694	0.529	0.367	0.294	0.285	0.275
5.0	0.727	0.547	0.367	0.286	0.277	0.264
6.0	0.773	0.574	0.373	0.283	0.271	0.257

pressure data for sodium bisulfite solutions in comparison to the relatively high accuracy of the isopiestic data for the other solutions. Therefore, it is estimated that the standard error of the activity-coefficient data for sodium sulfite and sodium bisulfite in sulfite-bisulfite solutions is about the same as that for the activity-coefficient data for sodium bisulfite in sodium bisulfite solutions, about 8%. Any error introduced by making the assumption that the activity coefficients of sodium sulfite in all of the sulfite-bisulfite solutions are equal to the activity coefficient of sodium sulfite in water at the same total ionic strength is well within this estimated standard error. The general consistency of the data as indicated by inspection of Figs. 7 and 8 and the fact that the Gibbs-Duhem equation was shown to be satisfied by the

final data are evidence of the general reliability of the data within the limits of accuracy specified.

SIGNIFICANCE OF THE ACTIVITY-COEFFICIENT DATA

There is a general pattern of behavior of the activity-coefficient data shown in Figs. 5 and 6. The convergence of the activity-coefficient data for electrolytes of a given valence type as the concentration approaches infinite dilution has been explained quite satisfactorily by the considerations involved in the derivation of the Debye-Hückel equation. However, even though it is recognized that such factors as the effective diameter of ions and the salting out effect contribute to the divergence of the activity-coefficient data at finite concentrations, there is presently no method by which the divergence of the data can be treated quantitatively.

When activity-coefficient data for a given electrolyte are desired and there are no data available, known activity-coefficient data for another electrolyte of similar valence type have often been used as a substitute. That is, it is assumed that the activity-coefficient data of the two electrolytes are similar. An example of this is assuming that the activity-coefficient data of sodium sulfite are similar to that of sodium sulfate. Figure 5 shows that this assumption is very good in dilute solutions and that the deviation of the data for sodium sulfite from that of sodium sulfate increases with concentration until at 2 molal, the sulfite data are about 10% higher than the sulfate data. Because of the similarity between the chemistry of sodium carbonate and

sodium sulfite, it might be supposed that the activity-coefficient data for sodium carbonate and sodium sulfite are quite similar. It is evident from Fig. 5 that there is a considerable difference in the data for these two salts. This observation suggests that the practice of substituting the activity-coefficient data of one electrolyte for that of another electrolyte can result in large errors. The error that can result from this practice is shown further by comparing the activity-coefficient data for lithium sulfate and sodium sulfate in Fig. 5; this comparison is even more significant when it is noted that the activity-coefficient data for sodium sulfate and potassium sulfate are nearly identical. However, in spite of the possibility of large errors introduced by this practice, the size of the errors so introduced is considerably smaller than the error introduced by the common practice of assuming activity coefficients equal to unity.

The value of the activity coefficient of sodium bisulfite at a given molality is lower than the corresponding value of the activity coefficient of any other inorganic 1:1 electrolyte for which activity-coefficient data were found in the literature. Because of the larger variation in the individual behavior of 1:1 electrolytes, the errors introduced by the practice of using the activity-coefficient data of one electrolyte to estimate the activity-coefficient data of another electrolyte in the case of the 1:1 electrolytes can be even larger than in the case of 1:2 electrolytes.

It is believed that the activity-coefficient data for sodium sulfite and sodium bisulfite in sodium sulfite-bisulfite solutions are the

first of their kind to be calculated from experimental data. Han and Bernardin (3) calculated the activity coefficients of sodium bicarbonate in sodium carbonate-bicarbonate solutions from an equation analogous to Equation (3):

$$\gamma_{HCO_3^-} = \left(\frac{K' \; a_{H_2O} \; a_{CO_2} \; m_{CO_3^=} \; \gamma_{CO_3^=}}{m^2_{HCO_3^-}} \right)^{1/2} \qquad (3')$$

The activity coefficient of sodium bicarbonate can be shown to be equal to the activity coefficient of bicarbonate ions by equations analogous to Equations (22) and (23) of Appendix IV. Thus, the activity coefficients of sodium bicarbonate can be calculated from this equation if the quantities on the right side of the equation can be evaluated.

Han and Bernardin evaluated each of these quantities at several temperatures as follows: 1) the equilibrium constant K' from data in the literature; 2) the activity of water a_{H_2O} by assuming that it is equal to its mole fraction in accordance with Raoult's law; 3) the activity of carbon dioxide a_{CO_2} from carbon dioxide vapor-pressure data for the sodium carbonate-bicarbonate system; 4) the molalities of carbonate and bicarbonate ions by stoichiometric calculations from assumed values of the fraction of sodium as bicarbonate and the total ionic strength, the calculation parameters; 5) the activity coefficients of carbonate ions from the activity-coefficient data for sodium carbonate by equations analogous to Equations (22) and (23)--according to these relationships the activity coefficient of carbonate ions is equal to the square of the activity coefficient of sodium carbonate.

It is evident that there are several questionable assumptions in this calculation procedure. The most serious of these are the assumptions of the relationships between the ionic and molal activity coefficients, and the assumption that the activity coefficients of the carbonate ions are not a function of the fraction of sodium as bicarbonate. It is not possible to assess the magnitude of the errors introduced into the calculations by these assumptions without additional experimental data. It should also be noted that it is possible that all of the assumptions are valid for the sodium carbonate-bicarbonate system.

The activity-coefficient data calculated by Han and Bernardin were obtained as a function of the fraction of sodium as bicarbonate and the total ionic strength. However, they reported the activity-coefficient data as a function of the total ionic strength only. The variation of the data with the fraction of sodium as bicarbonate was less than 5%; thus, these authors did not feel justified in reporting the data as a family of curves similar to the data for sodium bisulfite in Fig. 8 on the basis of their data alone because of the assumptions involved in their calculation procedure.

It is now possible to examine the activity-coefficient data for sodium bicarbonate in the light of the activity-coefficient data obtained in this study for sodium bisulfite and sodium sulfite. The activity-coefficient data for sodium bisulfite indicate that the variation of the activity-coefficient data of sodium bicarbonate with the fraction of sodium as bicarbonate is significant. Indeed, examination of the original plot of the bicarbonate data showed that a definite

and consistent variation exists in the individual data points with the fraction of sodium as bicarbonate comparable to that for sodium bisulfite. Furthermore, this plot also shows evidences of convergence of the family of curves at low concentrations and divergence at high concentrations similar to the data for sodium bisulfite. This convergence and divergence is more pronounced in the data for the activity coefficients at 50 and 65°C.

The variation of 5% in the activity-coefficient data of sodium bicarbonate with the fraction of sodium as bicarbonate is considerably smaller than the similar variation of 80% found for the sodium bisulfite data. If activity-coefficient data for carbonate ions having a variation with the fraction of sodium as bicarbonate comparable to that for sodium sulfite were used for the calculations, then the resulting activity-coefficient data for sodium bicarbonate would show a variation with the fraction of sodium as bicarbonate of up to 50%. It should be noted, however, that the amount of this variation cannot be inferred from the data on the sulfite-bisulfite system; it can only be said that a certain amount of variation is expected and that the amount of variation obtained for the activity coefficients of sodium bicarbonate is significant. The activity-coefficient data for sodium bicarbonate calculated from experimental measurements by Busche (4) indicate that the variation of the activity coefficients with the fraction of sodium as bicarbonate may be considerably smaller than the comparable variation obtained for sodium bisulfite.

Figures 7 and 8 show that the activity-coefficient data for both

sodium sulfite and sodium bisulfite converge at an ionic strength of about 0.5. In the case of the data for sodium sulfite, this convergence at a total ionic strength of 0.5 was forced by making the assumption that the activity coefficient of sodium sulfite in all the sulfite-bisulfite solutions is the same as the activity coefficient of sodium sulfite in pure solution at a total ionic strength of 0.5. However, this assumption does not affect the fact that the data converge; it affects only the point where the convergence occurs. The data for sodium bisulfite show that the well-known Lewis and Randall assumption, that the activity coefficients of an electrolyte in a mixed electrolyte solution are a function of the total ionic strength of the solution and not the kinds of ions present, holds for the sodium bisulfite data up to an ionic strength of about 0.5. However, above an ionic strength of 0.5, the use of this assumption could lead to an error of up to 70% in the activity coefficient. For example, at a total ionic strength of 4 and a value of the ratio of the total sulfur dioxide to total sodium of 0.6, the data of Fig. 8 show that the activity coefficient of sodium bisulfite is 0.529. Using the Lewis and Randall assumption, the value of the activity coefficient would be 0.275—this is low by 48%. If the Lewis and Randall assumption was not used and the activity coefficient taken as that for sodium sulfite in pure solution at the molality of sodium sulfite in the sulfite-bisulfite solution, the value of the activity coefficient would be 0.450. This value is only about 15% lower than the value of 0.529. In fact, the error that results from using the Lewis and Randall assumption is larger in all cases in this particular application. The convergence of the activity-coefficient data

is discussed further in the supplementary discussion of the results in Appendix VII.

It is evident from Fig. 7 that the activity coefficient of sodium sulfite increases as the ratio of total sulfur dioxide to total sodium increases or as the ratio of sodium bisulfite to sodium sulfite increases. If a fixed amount of a sodium sulfite solution of total ionic strength equal to 4 is taken and sufficient sodium bisulfite is added so that the resulting solution has a total ionic strength of 5, the activity of the sodium sulfite in the original solution and the activity of sodium sulfite in the final solution are considerably different. The molality of sodium sulfite in both solutions is 1.333; however, the activity coefficient of sodium sulfite is 0.20 in the original solution and 0.36 in the final solution. Thus, the activity of sodium sulfite in the final solution is 80% greater than the activity of sodium sulfite in the original solution. If a certain phenomenon like the rate of a chemical reaction were found to depend upon the activity of sodium sulfite in solution, the rate could be changed considerably by varying the amount of sodium bisulfite in the solution. This observation suggests the further possibility of making a desired change in the activity of one component of a solution by adding an additional, inert component to the solution.

CALCULATION OF WATER ACTIVITY

The water activity term, a_w, in the equilibrium equation, Equation (3), has already been evaluated for sodium bisulfite solutions and

sodium sulfite-bisulfite solutions in the calculation procedures just described. The standard error of the water activity data is about 0.8%.

CALCULATION OF THE EQUILIBRIUM CONSTANT

The equilibrium constant K of Equation (3) is equal to the ratio of K_1 and K_2, the first and second ionization constants of sulfurous acid. These ionization constants have been measured by several investigators (13, 21-23). There is general agreement among the values reported for K_1 with the exception of the value given by Tartar and Garretson (22). The value given by Sherrill and Noyes (23) was discarded because of the lower order of accuracy of their work. If, in addition, the value given by Tartar and Garretson is discarded, there are four values of K_1 remaining; these four values were derived from three different experimental methods. The mean of these four values is 0.0128 with a standard error of 2.3%. The discarding of the value given by Tartar and Garretson is justified since it is over 14 standard deviations away from the mean value of 0.0128. It is estimated that this value has a standard error of about 5%.

There are only two values of the second ionization constant reported in the literature that were obtained using methods of high accuracy. Both sources (21, 22) give 6.24×10^{-8} as the value of the second ionization constant. It is estimated that this value has a standard error of about 5%. The ratio of the two values, K_1/K_2, is 0.05×10^5; therefore, K equals 2.05×10^5 with a standard error of about 7%.

CALCULATION OF SULFUR DIOXIDE ACTIVITY

The activity of sulfur dioxide was calculated from Equation (13). The Henry's law constant was evaluated from literature data on the solubility of sulfur dioxide in water. Johnstone and Leppla (13) evaluated the Henry's law constant by calculating the activity of undissociated sulfur dioxide in water as a function of the partial pressure of sulfur dioxide above the solution. They determined the equilibrium solubility experimentally and used a value of the first ionization constant of sulfurous acid of 0.0130 in their calculations. They determined the value of the Henry's law constant to be 1.26 and found that the system follows Henry's law up to a partial pressure of sulfur dioxide of 1000 mm. of mercury. Parkison (24) has also measured the solubility of sulfur dioxide in water over the same low range of partial pressures at several temperatures. Parkison's data were plotted, interpolated at 25°C., and then plotted together with Johnstone and Leppla's data. The two sets of data agreed generally; Parkison's data were consistently about 5% higher. Therefore, one smooth curve was drawn to fit both sets of data and the Henry's law constant recalculated using the same method that Johnstone and Leppla used. The value of 0.0128 for K_1 evaluated above was used instead of 0.0130. The result was a value of 1.28 for the Henry's law constant. It is estimated that the standard error of this value of the Henry's law constant is about 5%.

The activity of sulfur dioxide in a sodium bisulfite solution is the product of the Henry's law constant and the vapor pressure of sulfur

dioxide above the solution. The measured vapor pressure of sulfur dioxide above sodium bisulfite solutions has already been discussed. No data are available on the vapor pressure of sulfur dioxide above sodium sulfite-bisulfite solutions at 25°C. Johnstone's data (5) for this system at 35°C. and higher temperatures were extrapolated to 25°C. and plotted together with the vapor-pressure data for sulfur dioxide above sodium bisulfite solutions obtained in this study. The accuracy of the extrapolated data and the amount of data are insufficient to make more than the following qualitative statements about the solutions at 25°C. The vapor pressure of sulfur dioxide:

1) increases with increasing total sodium;

2) increases with increasing ratio of total sulfur dioxide to total sodium;

3) is less than 1 mm. of mercury at values of the ratio of total sulfur dioxide to total sodium below 0.95;

4) is less than 0.5 mm. of mercury at values of the ratio of total sulfur dioxide to total sodium less than 0.9;

5) is less than 0.1 mm. of mercury at values of the ratio of total sulfur dioxide to total sodium less than 0.8.

CALCULATION OF THE EQUILIBRIUM COMPOSITION

COMPOSITION OF SODIUM BISULFITE SOLUTIONS

The equilibrium equation, Equation (3), was solved simultaneously with Equation (4) to obtain the concentration of sodium sulfite and sodium bisulfite in sodium bisulfite solutions. The results are given in Table IX and Fig. 9. The details of the calculation procedure are given in Appendix V.

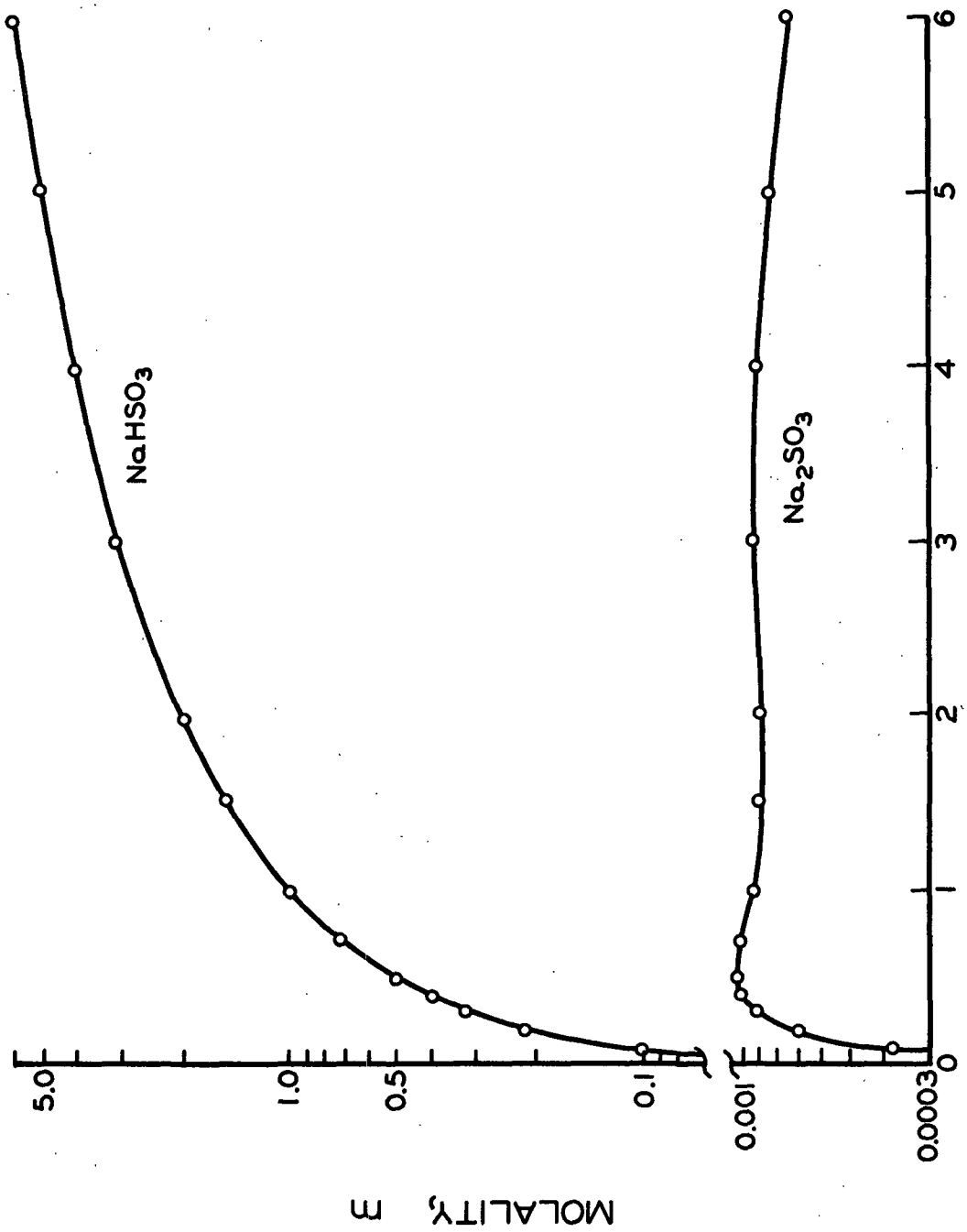

Figure 9. Composition of Sodium Bisulfite Solutions at 25°C.

TABLE IX

COMPOSITION OF SODIUM BISULFITE SOLUTIONS AT 25°C.

Molality Total Sodium	Molality Na_2SO_3	Molality $NaHSO_3$
0.1	0.000376	0.09924
0.2	0.000687	0.19863
0.3	0.000906	0.29819
0.4	0.001010	0.39798
0.5	0.001040	0.49792
0.7	0.001020	0.69796
1.0	0.000911	0.99818
1.5	0.000887	1.49823
2.0	0.000895	1.99821
3.0	0.000936	2.99813
4.0	0.000918	3.99816
5.0	0.000841	4.99832
6.0	0.000731	5.99854

Estimations of the standard errors of the molalities of sodium sulfite and sodium bisulfite were made by calculating the propagation of the errors of the individual quantities in the equilibrium equation. Thus, the standard error of the molality of sodium sulfite was estimated to be about 17% of all concentrations; the standard error of the molality of sodium bisulfite was estimated to be 0.2% for a 0.1 molal solution diminishing to about 0.003% for a 6 molal solution. This somewhat unusual result stems partly from the nature of the equilibrium equation and partly from the fact that the molality of sodium bisulfite is much larger than the molality of sodium sulfite. It should also be noted that the standard error of the sodium bisulfite molality is considerably smaller than the standard error of all of the other quantities in the equilibrium equation.

The assumption that the presence of constituents other than sodium bisulfite in a sodium bisulfite solution has no significant effect on the calculation of the activity coefficients of sodium bisulfite in a sodium bisulfite solution can now be validated. The validity of this assumption also affects the accuracy of the activity-coefficient data for sodium sulfite in a sodium bisulfite solution. The change in activity coefficients of both sodium sulfite and sodium bisulfite in sulfite-bisulfite solutions as the ratio of total sulfur dioxide to total sodium changes from 0.9 to 1.0 does not exceed 5%. The change from 0.9 to 1.0 in the total sulfur dioxide to total sodium ratio corresponds to a change from 0.27 to 0 in the quantity $\underline{x}_1$, the fraction of the total ionic strength attributed to sodium sulfite. The values of $\underline{x}_1$ calculated from the data in Table IX range from 0.011 to 0.00037. Thus, the error introduced in the calculated activity-coefficient data for sodium bisulfite and sodium sulfite in sodium bisulfite solutions by making the above assumption is well within the standard error of the activity coefficient data, 8%.

In very dilute solutions, where certain simplifying assumptions can be made, the pH of a sodium bisulfite solution can be calculated from the equilibrium data. The pH was evaluated from three equations: one based on the first ionization constant of sulfurous acid, one based on the second ionization constant of sulfurous acid, and one derived by eliminating the activity of bisulfite ions from the first two equations. The pH of a sodium bisulfite solution with the molality of total sodium equal to 0.1 (approximately 0.1 molal in sodium bisulfite), was calculated from the three equations; the resulting pH values were respectively:

4.21±0.06; 4.45±0.08; 4.33±0.08. The values after the plus and minus signs are equal to the standard errors. All of the calculated pH values lie within plus or minus two standard errors of each other. The measured value of the pH of a sodium bisulfite solution of this same concentration was 4.41±0.03; this measured value is in agreement with the calculated values plus or minus three standard errors. Therefore, in view of the assumptions involved in the calculated pH values, it is concluded that this agreement of measured and calculated pH values indicates that the data are reliable within the accuracy limits specified in the concentration range of 0.1 molal. The details of the pH calculations are given in Appendix V.

It is noted that the amount of sodium sulfite present in a sodium bisulfite solution is very small. The data show that at 0.1 molality of total sodium the dissociation of the sodium bisulfite is 0.8% with a standard error of 0.17%. The maximum probable percent dissociated, that is the percentage dissociated plus three standard errors, is 1.3%. The relative amount of dissociated bisulfite decreases as the concentration increases so that at a molality of total sodium of 6 the dissociation is 0.03 with a standard error of 0.003%.

The constituents present in a sodium bisulfite solution other than sodium sulfite and sodium bisulfite are dissolved sulfur dioxide, hydrogen and bisulfite ions from the ionization of the dissolved sulfur dioxide (sulfurous acid), and hydrogen and hydroxyl ions from the ionization of water. The concentrations of hydrogen and bisulfite ions from the ionization of the dissolved sulfur dioxide are equal. Also, it is

evident from Equation (2) that the concentration of dissolved sulfur dioxide would equal the concentration of sodium sulfite if none of the dissolved sulfur dioxide were ionized. Therefore, the concentration of dissolved sulfur dioxide plus the concentration of the hydrogen ions (or the bisulfite ions) from the ionization of the dissolved sulfur dioxide must equal the concentration of sodium sulfite. Since the solution contains a relatively large number of bisulfite ions from the sodium bisulfite, the presence of the additional bisulfite ions from the ionization of sulfur dioxide is of little consequence. Also, the concentration of hydroxyl ions in the solution is negligibly small.

Thus, the total number of moles of constituents other than sodium bisulfite in the solutions equals twice the number of moles of sodium sulfite. Therefore, at a total sodium molality of 0.1, about 0.8% of the sodium bisulfite is dissociated producing about 0.8 mole percent of constituents other than sodium bisulfite; these values decrease with increasing concentration so that when the total sodium molality is 6.0, about 0.03% of the sodium bisulfite is dissociated producing about 0.03 mole percent of constituents other than sodium bisulfite. Calculation of the concentrations of dissolved sulfur dioxide and hydrogen ions is not possible since the activity coefficients of the ions are not known.

COMPOSITION OF SODIUM SULFITE SOLUTIONS

The composition of a sodium sulfite solution cannot be calculated from the equilibrium equation because the activity of sulfur dioxide in sodium sulfite solutions is not known. The activity of sulfur dioxide was estimated from Equation (29) of Appendix V to be about 3×10^{-14} for

a 0.0333 molal sodium sulfite solution. This corresponds to a sulfur dioxide vapor pressure of about 2×10^{-11} mm. of mercury—a vapor pressure virtually immeasurable by any presently known method. However, the composition can be estimated from the degree of hydrolysis. The degree of hydrolysis of the sodium sulfite in a 0.1 molal sodium sulfite solution is about 0.1%; the degree of hydrolysis decreases with increasing concentration until at 2 molal it is 0.007%. (The degree of hydrolysis is calculated in Appendix IV.) One mole of sodium sulfite hydrolyzes to produce one mole each of sodium bisulfite and sodium hydroxide. Therefore, in a 0.1 molal solution of sodium sulfite, where the degree of hydrolysis is about 0.1%, the mole percent of sodium bisulfite and sodium hydroxide in the solution will be 0.1% assuming no dissociation of the sodium bisulfite. Since some of the sodium bisulfite will dissociate according to Equation (2), the sum of all of the constituents other than sodium sulfite in the solution will be less than 0.2 mole percent. The small number of hydrogen and hydroxyl ions from the ionization of water is assumed to be negligibly small. Therefore, a 0.1 molal sodium sulfite solution has a degree of hydrolysis of about 0.1% with the products of hydrolysis comprising less than 0.2 mole percent of the total moles of constituents in the solution; these quantities decrease as the concentration increases so that at 2 molal, the sodium sulfite solution has a degree of hydrolysis of 0.007% with the products of hydrolysis comprising less than 0.015 mole percent of the total moles of constituents in the solution.

COMPOSITION OF SODIUM SULFITE-BISULFITE SOLUTIONS

The composition of the various sodium sulfite-bisulfite solutions cannot be calculated because only qualitative sulfur dioxide vapor-pressure data are available. However, it can be shown by qualitative reasoning, (see Appendix VI), that the portion of sodium bisulfite dissociated decreases rapidly as the ratio of total sulfur dioxide to total sodium decreases from 1.0 toward 0.5. Thus, at a ratio of total sulfur dioxide to total sodium of 0.9 it was estimated that the portion of sodium bisulfite dissociated is less than 0.1%. It can also be said with some confidence that almost all of the decrease in the portion of sodium bisulfite dissociated takes place in the range of total sulfur dioxide to total sodium from 1.0 to 0.95. Therefore, it is concluded that: 1) When the total sulfur dioxide to total sodium ratio is less than 0.9, the dissociation of sodium bisulfite is less than 0.1%, and that the relative amounts of sodium sulfite and sodium bisulfite present are essentially the same as the amounts calculated stoichiometrically; 2) When the ratio of total sulfur dioxide to total sodium is between 0.9 and 0.95, the dissociation of sodium bisulfite is estimated to be less than 0.2%; 3) When the ratio of total sulfur dioxide to total sodium is between 0.95 and 1.0, the percent of dissociation of sodium bisulfite has values between the percentages dissociated at ratios of total sulfur dioxide to total sodium of 0.95 and 1.0. The concentrations of the minor constituents can be shown to be quite negligible for most of the sulfite-bisulfite solutions; where the concentrations are not negligible, they can be inferred from the previous discussions of the compositions of sodium sulfite and sodium bisulfite solutions.

SIGNIFICANCE OF THE EQUILIBRIUM COMPOSITION DATA AND SUGGESTIONS FOR FUTURE STUDY

It is believed that this study on the system sodium sulfite-sodium bisulfite-water represents the first attempt to make a thermodynamic study of mixed electrolyte solutions involving chemical reaction. The thermodynamic data obtained in this study have been used either to calculate or estimate the equilibrium composition of the various solutions of the system. This is particularly significant when it is realized that there is no known analytical method whereby the composition of a mixed electrolyte solution involving chemical reaction can be ascertained.

It might be concluded that the small difference between the composition of the solutions of the system arrived at in this study and the composition calculated from purely stoichiometric considerations is of little consequence. This conclusion may well be valid for some applications of the data; however, for equilibrium applications, no quantity that is present in the equilibrium relationships can be neglected. For example, it was estimated that the activity of sulfur dioxide in a 0.0333 molal sodium sulfite solution was 3×10^{-14}. The magnitude of this quantity is negligibly small; however, because of the mathematical nature of the equilibrium equation, Equation (3), it cannot be neglected in considerations of the equilibria in sodium sulfite solutions.

The importance of the minor constituents in a sodium sulfite solution can be illustrated further by considering the Arbiso pulping process

(20). It is claimed that the Arbiso process, a process for pulping using sodium bisulfite solutions as the pulping liquor, is distinguished from the normal acid sulfite pulping process by the absence of sulfur dioxide in the cooking liquor. That this claim is fallacious is evident from previous discussion of the composition of sodium bisulfite solutions. It has been suggested that the active agent in acid sulfite pulping is sulfurous acid. If this is also true for the Arbiso process, then it follows that the presence of small amounts of dissolved sulfur dioxide may be the most important part of the system from a pulping viewpoint.

The methods of calculation used in this study have indicated the general usefulness of the McKay-Perring equation for the calculation of activity coefficients of the constituents of mixed electrolyte solutions. Indeed, the most promising approach to further study of complex electrolyte solutions appears to be the application of the McKay-Perring equation to isopiestic vapor-pressure data. The outstanding advantages of this approach are: 1) the ease with which isopiestic data of high accuracy can be obtained; 2) the applicability of the McKay-Perring equation to systems containing any number of constituents; 3) the possibility of obtaining activity-coefficient data for an electrolyte which cannot be prepared in pure solution. There are two disadvantages to the approach: 1) tedious, iterative calculation procedures are required; 2) evaluation of the integrals when the lower limit of integration is infinite dilution may be uncertain. The first disadvantage can be offset somewhat by the use of electronic computing devices. Obtaining careful isopiestic measurements on very dilute solutions may completely eliminate the second disadvantage for many systems.

In order to apply this approach to complex systems having volatile solutes, the isopiestic technique must be suitably modified. It appears as though the problem of volatile solutes could be handled by knowing the vapor pressures of the volatile constituents; by modifying the isopiestic procedure to account for the amounts of the volatile constituents removed from the equilibration vessel during evacuation, and the amounts present in the vapor space inside the equilibration vessel; and by determining the effect of the presence of the volatile constituents on the activity of the reference electrolyte.

The need for extending thermodynamic studies to systems under the conditions of temperature and pressure encountered in the processes of the industry is quite evident. It appears that this same approach is also the most promising in this case. In fact, since the equilibration vessel will have to be under pressure for isopiestic measurements at high temperatures, it may be no longer desirable to evacuate the equilibration vessel and thus the procedure would be simpler.

An example of a complex system that could be studied by the above approach is a neutral sulfite semichemical pulping solution. This pulping solution contains various amounts of sodium sulfite, sodium bisulfite, sodium carbonate, sodium bicarbonate, sodium sulfate and sodium thiosulfate. If the system is simplified somewhat by leaving out the last two constituents listed, then the system is defined at constant temperature and total pressure by specifying the total sodium, the ratio of total sulfur dioxide to total sodium, and the ratio of total carbon dioxide to total sodium. The isopiestic data could be measured by

preparing a series of stock solutions with various ratios of total sulfur dioxide to total sodium and total carbon dioxide to total sodium, and equilibrating these solutions several at a time with the same reference electrolyte. That is, several different stock solutions would be diluted to the same concentration level and equilibrated at the same time with the reference solution. The activity coefficients of all the constituents in the solution could be calculated from this isopiestic data using the McKay-Perring equation. The equilibrium composition of the pulping solution could be calculated from the appropriate chemical equilibria equations.

The determination of the activity data for and the equilibrium compositions of complex electrolyte solutions provides information which is prerequisite for much-needed research in many areas of pulp and paper technology. The accumulation of such information will permit the studying of many problems in the areas of chemical reaction kinetics, chemical recovery, gas absorption and process design.

There is a supplementary discussion of the calculated results in Appendix VII.

SUMMARY AND CONCLUSIONS

1. The mean ionic molal activity coefficients of sodium sulfite in aqueous sodium sulfite solutions were calculated from isopiestic vapor-pressure data at 25°C. The calculations were made using an integrated form of the Gibbs-Duhem equation and an extended form of the Debye-Hückel equation. The activity-coefficient data covered a range of concentrations from 0.0333 to 2.0 molal. The standard deviation of the activity-coefficient data was estimated to be less than 0.5%.

2. The mean ionic molal activity coefficients of sodium bisulfite in aqueous sodium bisulfite solutions were calculated from data for the vapor pressure of water above sodium bisulfite solutions at 25°C. The calculations were made using a form of the McKay-Perring equation. It was shown that the presence of constituents in the bisulfite solution other than sodium bisulfite had no significant effect on the values of the calculated activity coefficients. The activity-coefficient data covered a range of concentrations from 0.1 to 7.0 molal. The standard deviation of the activity-coefficient data was estimated to be about 8%.

3. The activity coefficients of sodium sulfite and sodium bisulfite in aqueous sodium sulfite-bisulfite solutions were calculated as a function of the total ionic strength and the ratio of total sulfur dioxide to total sodium at 25°C. The data used for the calculations were the isopiestic data for sodium sulfite solutions and for sodium sulfite-bisulfite solutions with a molal ratio of sulfite to bisulfite of one, and the water vapor-pressure data for sodium bisulfite solutions. The calculations were made using two forms of the McKay-Perring equation.

The activity-coefficient data covered a range of concentrations from 0.1 to 6.0 total ionic strength and a range of ratios of the total sulfur dioxide to total sodium from 0.5 to 1.0. The standard deviation of the activity-coefficient data was estimated to be about 8%.

4. The compositions of sodium sulfite solutions, sodium bisulfite solutions and the various sodium sulfite-bisulfite solutions were determined from the chemical equilibria equations for the sodium sulfite-bisulfite system and various material balance equations. The final conclusions were:

a) Sodium sulfite solutions. A 0.1 molal solution has a degree of hydrolysis of about 0.1% with the products of hydrolysis comprising less than 0.2 mole percent of the total moles of constituents in the solution; these quantities decrease as the concentration increases so that, at 2 molal, the sodium sulfite solution has a degree of hydrolysis of 0.007% with the products of hydrolysis comprising less than 0.01% of the total moles of constituents in the solution.

b) Sodium bisulfite solutions. In a solution with a molality of total sodium of 0.1, about 0.8% of the sodium bisulfite is dissociated producing about 0.8 mole percent of constituents other than sodium bisulfite; these values decrease with increasing concentration so that when the total sodium molality is 6.0, about 0.03% of the sodium bisulfite is dissociated producing about 0.03 mole percent of constituents other than sodium bisulfite.

c) Sodium sulfite-bisulfite solutions. (1) When the total sulfur dioxide to total sodium ratio is less than 0.9, the dissociation of sodium bisulfite is less than 0.1%. (2) When the ratio of total sulfur dioxide to

total sodium is less than 0.95, the dissociation of sodium bisulfite is less than 0.2%. (3) When the ratio of total sulfur dioxide to total sodium is between 0.95 and 1.0, the percentage of dissociation is between 0.2 and 0.8%.

5. The general reliability of the experimental and calculated results were shown in several ways. No indications of any internal inconsistencies in the results or general thermodynamic discrepancies were found. The thermodynamic significance of the results were discussed in the light of their contribution to the knowledge of the thermodynamic behavior of electrolyte solutions, other data in the literature, the work of Han and Bernardin on the sodium carbonate-bicarbonate system, the importance of knowing the composition of mixed electrolyte solutions involving chemical reaction, and possibilities for future study of more complex systems.

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APPENDIX I

ISOPIESTIC MEASUREMENTS ON SODIUM SULFITE SOLUTIONS

The isopiestic vapor-pressure comparison technique was used to obtain data from which the activity coefficients of sodium sulfite in aqueous solution could be calculated. The apparatus and procedure used were essentially the same as those used by Sinclair (14), and Robinson and Sinclair (15).

APPARATUS

The apparatus that was used is similar to that used by most investigators using the isopiestic technique. The equilibration vessel was a 160-mm. vacuum desiccator. A silver-plated disk of high conductivity copper was turned so that it fitted inside of the desiccator on the ledge upon which the plate usually rests. A molten mixture of wax and brass turnings was placed in the lower part of the desiccator, the space which normally contains the desiccant, in an amount sufficient to completely fill this space and to produce a tight seal between the disk and the desiccator.

The solutions to be equilibrated were placed in dishes turned from a rod of fine silver 4.5 cm. in diameter. The finished dishes were 2 cm. high with an inside diameter and inside depth of 3.8 and 1.8 cm., respectively. The bottoms of the dishes and the top surface of the disk were turned very flat to insure good contact when the dishes were placed on the disk for the equilibration. Small cubes of one-quarter inch lucite, faced with cotton flannel, were glued to the surface of the disk to

prevent the dishes from sliding. Each determination was made in triplicate using six dishes; one solution was placed in three dishes and the other solution was placed in the remaining three dishes. The six dishes were arranged in a circular pattern on the disk so that a dish containing one solution was between two dishes containing the other solution. Each dish was fitted with a lucite lid for use during the filling and weighing steps of the procedure.

The equilibration was carried out in a constant temperature bath controlled to 25.000±0.005°C. A rocking mechanism was constructed so that the desiccator was rocked through a total angle of 20 degrees at a frequency of 60 cycles per minute during the equilibration. This rocking action insured complete mixing of the solutions at all times.

Because of the rapid oxidation of sulfite and bisulfite solutions by atmospheric oxygen, a nitrogen chamber was constructed in which the procedural steps that involved exposure of the solutions to the atmosphere were carried out. Provision for introducing and removing items from the chamber was made by constructing a water-purged air lock on one end. An analytical balance was placed inside the chamber together with other necessary apparatus. The oxygen level of the nitrogen in the chamber was maintained below 2000 p.p.m. by circulating the chamber nitrogen through an oxygen removal system (25). The nitrogen in the chamber was kept under a positive pressure of about one-quarter inch of water at all times.

PROCEDURES

PREPARATION OF SOLUTIONS

The sodium chloride reference solutions were prepared from Baker's reagent-grade sodium chloride and conductivity water. The sodium chloride had a lot analysis of 99.9% NaCl and was dried overnight at 110°C. before using. The water was prepared by passing distilled water through Amberlite MB-3 exchange resin; the specific resistance of this water was about three million ohms-centimeters. About 60 grams of six molal sodium chloride solution were prepared gravimetrically as a stock solution and stored in a polyethylene bottle. The stock sodium chloride solution was diluted to the desired concentration for each isopiestic determination.

The sodium sulfite solutions were prepared by adding measured amounts of sulfur dioxide gas to sodium hydroxide solutions. A stock sodium hydroxide solution was prepared by adding deaerated water to deoxygenated Baker's reagent-grade 50% sodium hydroxide solution; the 50% solution had a lot analysis of 0.02% carbonate. The water was deaerated by boiling under vacuum for 30 minutes, and the 50% caustic solution was deoxygenated by vigorously bubbling nitrogen through the solution for at least one hour. The strength of the stock sodium hydroxide solution was determined by titrating an aliquot of the solution with standard acid. During the preparation and handling of these solutions, oxygen contamination was kept at a minimum by keeping the solutions in closed polyethylene bottles under nitrogen.

The stock sodium hydroxide solution was placed in the nitrogen chamber. About 100 grams of the solution were transferred to a tared polyethylene bottle and further diluted with about 25 grams of oxygen-free water. This bottle was fitted with two glass tubes through a rubber stopper so that sulfur dioxide gas could be bubbled into the solution near the bottom of the bottle and so that the vapor space above the solution was vented. Ansul refrigeration-grade sulfur dioxide was bubbled into the sodium hydroxide solution until a slight excess of sulfur dioxide was added above the amount required for complete conversion of hydroxide to sulfite. The sulfur dioxide had a manufacturer's assay of 99.98% SO_2. The amount of excess sulfur dioxide was determined and a sufficient amount of dilute sodium hydroxide solution was added to exactly balance the excess sulfur dioxide. All determinations in the above steps were made gravimetrically. The final sodium sulfite solution was used as a stock solution and diluted to the desired concentration for each isopiestic determination.

A sample calculation is now given to illustrate this preparation procedure:

1) Stock sodium hydroxide solution

Weight of 50% sodium hydroxide solution: 190 g.

Weight of deaerated water: 310 g.

Weight of aliquot taken for titration: 17.300 g.; aliquot then diluted to one liter

Volume of 0.09630N acid required to titrate 25.00 ml. of diluted aliquot: 20.62 ml.

Milliequivalents of NaOH per gram of stock sodium hydroxide solution:

$$\frac{(20.62)(0.09630)(1000)}{(25.00)(17.3000)} = 4.5914$$

2) Sodium hydroxide solution for sodium sulfite preparation

Weight of stock sodium hydroxide solution used: 100.7522 g.

Weight of oxygen-free water added: 27.1770 g.

Milliequivalents of sodium hydroxide per gram of this solution:

$$\frac{(4.5914)(100.7522)}{(100.7522 + 27.1770)} = 3.6160$$

3) Sodium sulfite solution (solution number 4)

Weight of sodium hydroxide solution to be treated with sulfur dioxide:

$$100.7522 + 27.1770 = 127.9292 \text{ g.}$$

Weight of sulfur dioxide required to convert sodium hydroxide to sodium sulfite:

$$\frac{(3.6160)(127.9292)(32.033)}{(1000)} = 14.8182$$

where 32.033 is the equivalent weight of sulfur dioxide. The sulfur dioxide is assumed to be 100% SO_2.

Weight of sulfur dioxide actually added: 14.8542 g.

Total weight of solution before bubbling tubes removed:

$$127.9292 + 14.8542 = 142.7834 \text{ g.}$$

Weight of solution lost with the removal of the bubbling tubes: 0.2396 g.

Total weight of solution after removal of bubbling tubes:

$$142.7834 - 0.2396 = 142.5438 \text{ g.}$$

Milliequivalents of NaOH per gram of solution after sulfur dioxide addition:

$$\frac{(3.6160)(127.9292)}{(142.7834)} = 3.2398$$

Weight of sulfur dioxide added corrected for solution lost with removal of bubbling tubes:

$$\frac{(14.8542)(142.5438)}{(142.7834)} = 14.8293 \text{ g.}$$

Excess sulfur dioxide corrected for same loss:

$$\frac{(14.8542 - 14.8182)(142.5438)}{(142.7834)} = 0.03594 \text{ g.}$$

Weight of 0.8276 molal sodium hydroxide solution required to balance excess sulfur dioxide:

$$\frac{(0.03594)\qquad(1000)}{(32.033)(0.82760)} = 1.3557 \text{ g.}$$

Weight of 0.8276 molal sodium hydroxide solution actually added: 1.3516 g.

Total moles of NaOH present in final solution:

$$(3.2398)(142.5438)(1/1000) = 0.46181$$
$$(1.3516)(0.82760)(1/1000) = 0.00112$$

$$0.46181 + 0.00112 = 0.46293 \text{ moles}$$

Total moles of SO_2 present in final solution:

$$14.8293/64.066 = 0.23147 \text{ moles}$$

where 64.066 is the molecular weight of sulfur dioxide.

Ratio of NaOH to SO_2:

$$0.46293/0.23147 = 1.9996$$

Weight of Na_2SO_3 present in final solution:

$$(0.23147)(126.06) = 29.1791 \text{ g.}$$

where 126.06 is the molecular weight of sodium sulfite.

Total weight of final solution:

$$142.5438 + 1.3516 = 143.8954 \text{ g.}$$

Molality of sodium sulfite solution:

$$\frac{(0.23147)(1000)}{(143.8954 - 29.1791)} = 2.0178$$

In order to improve the reproducibility of the isopiestic data, the volumetric method used to determine the concentration of the stock sodium hydroxide solution was changed to a gravimetric method. About five grams of the sodium sulfite solution were placed in a tared porcelain crucible. Sufficient 1:10 sulfuric acid was added to produce about a 25% excess of acid above that required to convert all of the sodium to sodium sulfate. The moisture was removed by careful heating on a steam bath. When the contents of the crucible appeared dry, the excess acid was removed by fuming using a small Bunsen flame. When the fuming ceased, the crucible was placed in an electric furnace at 600°C. and heated to constant weight. The determinations were made in triplicate.

Because the results of the gravimetric sodium determination revealed an error in the concentration of the stock sodium hydroxide solution, it was necessary to readjust the sodium hydroxide-sulfur dioxide ratio of the sodium sulfite solutions. The procedure was the same as that already described; the sample calculation of solution number 4 is continued.

4) Readjustment of sodium sulfite solution (solution number 4)

New value for milliequivalents of NaOH per gram of stock sodium hydroxide solution: 4.6037

New value for molality of dilute sodium hydroxide solution used to balance excess sulfur dioxide: 0.82992

New value for total moles of NaOH present in final solution: 0.46417

New value for ratio of NaOH to SO_2: 2.0053

Weight of sodium sulfite solution to be readjusted: 129.7658 g.

Moles of NaOH present in this solution:

$$\frac{(0.46417)(129.7658)}{(143.8954)} = 0.41859$$

Moles of SO_2 present in this solution:

$$\frac{(0.23147)(129.7658)}{(143.8954)} = 0.20874$$

Weight of additional sulfur dioxide required to convert excess sodium hydroxide to sodium sulfite:

$$(0.41259/2 - 0.20874)(64.066) = 0.0356 \text{ g.}$$

Weight of sulfur dioxide actually added: 0.1543 g.

The remaining steps are similar to those just described leading to a final ratio of NaOH to SO_2: 1.99991

Molality of sodium sulfite solution: 1.9592

ISOPIESTIC DATA

A set of isopiestic data was obtained by equilibrating sodium sulfite solutions with sodium chloride solutions. The silver dishes with lids in place were first tared. Then a suitable quantity of stock sodium sulfite solution was added to three dishes and a suitable quantity of stock sodium chloride solution to the other three dishes, and each dish was weighed again. An appropriate amount of water was added to each

dish to produce approximately the desired concentration level. The total volume of solution in each dish was kept at about two milliliters. The dishes were placed in the desiccator, the lids of the dishes removed, and the cover placed on the desiccator. The pressure inside the desiccator was reduced gradually over a period of 30 minutes to a final value of 20 to 25 millimeters of mercury.

The evacuated desiccator was placed in the rocking mechanism in the constant temperature bath and equilibrated for at least 24 hours. Periods of equilibration up to several days were required for the most dilute solutions. Immediately after the desiccator was removed from the bath, the desiccator was filled with nitrogen and placed back in the nitrogen chamber. The lids of the dishes were replaced after the desiccator cover was removed and each dish was weighed again.

It was noticed during preliminary work that the tare weight of the lids of the dishes changed a small amount from day to day. Therefore, the lids were tared each time the dishes were weighed.

A sample calculation is now given to illustrate this procedure:

1) Sodium sulfite solutions (Run 43)

Tare of dish 1: 115.8960 g.

Weight of dish 1 after stock sodium sulfite solution added: 117.6565 g.

Weight of lid of dish 1: 10.3736 g.

Weight of dish 1 after equilibration: 118.1692 g.

Weight of lid of dish 1: 10.3716 g.

Weight of stock sodium sulfite solution added to dish 1:

$$117.6565 - 115.8960 = 1.7605 \text{ g.}$$

Weight of dilution water:

$$118.1692 - 117.6565 = 0.5127 \text{ g.}$$

Change in weight of lid:

$$10.3736 - 10.3716 = 0.0020 \text{ g. decrease}$$

Molality of final sodium sulfite solution in dish 1:

$$\frac{(1.7605)(0.19806)(1/126.06)}{1.7605 - (1.7605)(0.19806) + 0.5127 + 0.0020} = 1.4358$$

(The concentrated sodium sulfite solution contained 0.19806 grams of Na_2SO_3 per gram of solution.)

Similarly,

Molality of final sodium sulfite solution in dish 2: 1.4350

Molality of final sodium sulfite solution in dish 3: 1.4375

Average molality of these solutions: 1.4361

Standard deviation of this mean value: 0.07%

2) Sodium chloride solutions

Tare of dish 4: 117.6388 g.

Weight of dish 4 after stock sodium chloride solution added: 118.1811 g.

Weight of lid of dish 4: 10.4622 g.

Weight of dish 4 after equilibration: 119.2989 g.

Weight of lid of dish 4: 10.4594 g.

Weight of stock sodium chloride solution added to dish 4:

$$118.1811 - 117.6388 = 0.5423 \text{ g.}$$

Weight of dilution water:

$$119.2989 - 118.1811 = 1.1178 \text{ g.}$$

Change in weight of lid:

$$10.4622 - 10.4594 = 0.0028 \text{ g. decrease}$$

Molality of final sodium chloride solution:

$$\frac{(0.5423)(0.25764)(1/58.454)}{0.5423 - (0.5423)(0.25764) + 1.1178 + 0.0028} = 1.5692$$

where 58.454 = molecular weight of sodium chloride. (The concentrated sodium chloride solution contained 0.25764 grams of NaCl per gram of solution.)

Similarly,

Molality of final sodium chloride solution in dish 5: 1.5725

Molality of final sodium chloride solution in dish 6: 1.5718

Average molality of these solutions: 1.5712

Standard deviation of this mean value: 0.06%

When the isopiestic concentrations were greater than 0.5 molal, a run was rejected on the basis of failure to reach equilibrium in the allotted time if the standard deviation of the isopiestic concentration of one of the solutions was greater than 0.1%. It was necessary to accept slightly greater standard deviations when the concentrations were below 0.5 molal because of the magnification of errors at these low concentrations.

APPENDIX II

VAPOR-PRESSURE MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

APPARATUS

The apparatus used for the vapor-pressure measurements on sodium bisulfite solutions is shown schematically in Fig. 10. The two bottles A and B were arranged so that the water in A was connected to the water in B through the syphon line shown. The space above the water in the bottle B was filled with prepurified nitrogen. The nitrogen in B flowed out of B under the pressure of the head of water in A through the two gas washing bottles C and D. C and D contained concentrated sulfuric acid to dry the nitrogen.

Mounted in the constant temperature bath E were a three-necked flask F and six equilibrium tubes G. The three-necked flask was fitted with a mercury-sealed stainless steel stirring rod. The dry nitrogen entered the flask through one neck by means of a delivery tube extending to the bottom of the solution in the flask as shown. Four deep dimples were made in the side of the flask so that when the stirrer was turning there was good vapor-liquid contact. The six equilibrium tubes were connected in series to the nitrogen stream exit line of the three-necked flask. These tubes are described in detail by both Taylor and Johnstone; they are essentially just a means of providing nonviolent vapor-liquid contact with a minimum pressure drop. The vapor phase passed in small bubbles through the successive portions of the bisulfite solution in these tubes and then entered the Vanier bulb H. The exit

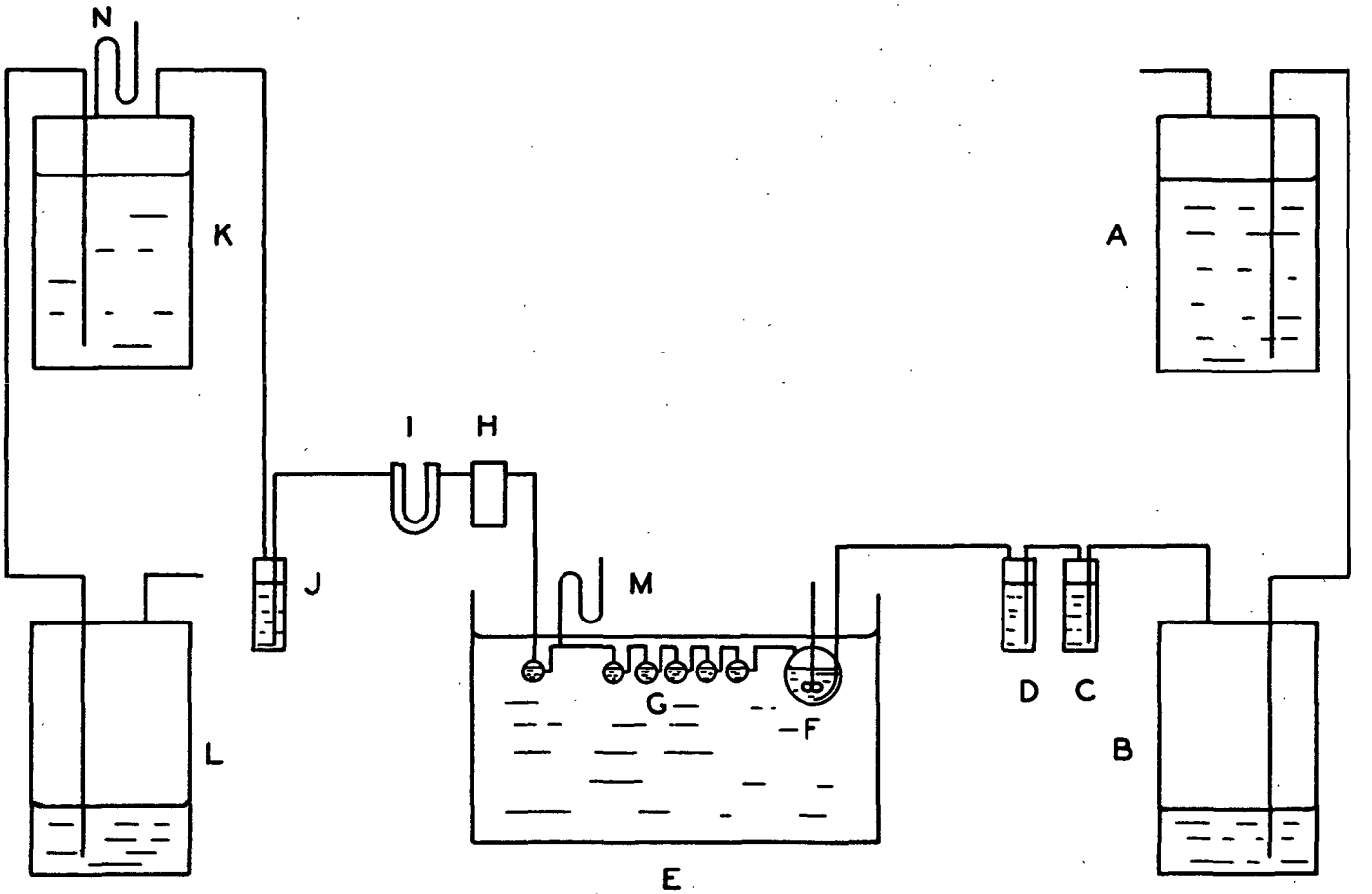

Figure 10. Vapor Pressure Apparatus

line from the last equilibrium tube was heated to prevent any condensation of the water vapor in the nitrogen stream. The Vanier bulb quantitatively removed the water vapor and sulfur dioxide from the nitrogen stream. The pure nitrogen then passed through the protective "U" tube I containing magnesium perchlorate, a humidifying gas washing bottle J containing water, and finally was collected in the bottle K. Bottle K was connected through a syphon line to bottle L so that a vacuum was produced in K as the water from K was allowed to flow into L.

The Vanier bulb is described in detail by Johnstone. It is basically a small bottle with a stopcock for a stopper. The bottle is divided into two compartments. The inner compartment contained magnesium perchlorate; the outer compartment contained a dilute sodium hydroxide solution. The nitrogen stream containing sulfur dioxide and water vapor passed first through the outer compartment for the removal of the sulfur dioxide, and then through the inner compartment for the removal of the water vapor. It was necessary to be able to reproducibly weigh the bulb to the nearest 0.1 mg. in order to determine the total mass of sulfur dioxide and water vapor absorbed during a run with the desired accuracy. This was accomplished by treating the exterior surface of the bulb with Desicote, by handling the bulb only with cotton gloves, by keeping the case of the analytical balance at nearly constant humidity, and by making successive weighings with the bulb in the case until the bulb came to constant weight. A similarly shaped and prepared bottle was used as a tare weight. The case of the balance was kept at nearly constant humidity by placing 16 culture dishes containing saturated magnesium chloride solutions inside the case. The Vanier bulb was

connected to the exit line of the last equilibrium tube with a ball and socket glass joint. It was found that the stopcock grease could be completely wiped off of the ball with paper towels.

There was a water manometer M connected between the fifth and sixth equilibrium tubes. Also, there was a manometer N connected to the vapor space of bottle K. Bottle K contained two thermometers mounted so that one extended down near the bottom of the bottle and the other one extended only a short distance from the top of the bottle. These thermometers were used to measure the temperature of the water and collected nitrogen in the bottle. All of the connections outside of the bath were made with combinations of glass and tygon tubing. All of the connections from the three-necked flask to the Vanier bulb were made with glass tubing fitted with glass ball and socket joints. A screw clamp was placed on the tygon tubing connecting the Vanier bulb and the "U" tube; this clamp was adjusted to keep the flow of the nitrogen stream uniform through the equilibrium tubes and the Vanier bulb. The temperature of the bath was maintained at 25.00 ± 0.05°C.

PROCEDURE

A stock sodium bisulfite solution was prepared in the same manner as the sodium sulfite solutions. About 8 kilograms of the stock solution were prepared and diluted to the concentration desired for each run. The dilute solutions were prepared with deaerated water; suitable precautions were taken to keep the oxygen exposure to a minimum. One-tenth percent of hydroquinone were added to the stock sodium bisulfite solution to inhibit oxidation. The apparatus was prepared for a run by

placing about 350 ml. of the bisulfite solution in the three-necked flask and about 200 ml. of the solution in each of the six equilibrium tubes. The three-necked flask was flushed with nitrogen and then the bisulfite solution was added to the flask; the solution was added from a closed bottle by forcing the solution out with nitrogen. Each equilibrium tube was filled in succession in a similar manner. The nitrogen was flushed continually through the system while the tubes were being connected; each tube was allowed to flush for about five minutes before being connected to the next tube.

The Vanier bulb was prepared by charging it with magnesium perchlorate and 0.2N sodium hydroxide solution. The measurement of the total pressure in the sixth equilibrium tube by the manometer M required the determination of the head of bisulfite solution in the sixth equilibrium tube. This determination was made by reading the manometer M while the nitrogen stream was being vented to the atmosphere. About 40 ml. of the sodium hydroxide solution were added to the bulb and then prepurified nitrogen was passed through the bulb to flush it clear of air. Then the bulb was placed in the balance case until it came to constant weight. This usually required from 2 to 3 hours. About 30 minutes before the Vanier bulb was weighed for the last time and placed into the vapor-pressure apparatus, the nitrogen flow was started and the apparatus operated in the same manner as when an actual run was being made. During this preliminary period, the nitrogen was vented to the atmosphere by the exit line from the last equilibrium tube. Also, during this period, the bottle K was filled completely with water and weighed, and the temperature of the water in the bottle was recorded.

The bulb was weighed, placed in a plastic bag and connected into the apparatus. The nitrogen flow rate, the reading on manometer M and the barometric pressure were read at frequent intervals of time so that the average pressure could be calculated. The nitrogen flow rate was determined by counting the bubbles per minute of nitrogen that passed through the gas washing bottle D. The flow rate of nitrogen entering the three-necked flask and the flow of water from the bottle K were adjusted to keep the manometer M reading less than 12 inches of water pressure. The nitrogen flow rate used for most of the runs was about 1000 cc. per hour. The runs on the dilute solutions were made for four hours; the duration of the run was decreased as the concentration increased until the runs for the most concentrated solutions were made for three hours. The reading of manometer N and the level of the water in bottle A were recorded to aid in control.

After the desired amount of nitrogen had been passed through the apparatus, the Vanier bulb was removed from the apparatus, briefly opened to the atmosphere to release any pressure and placed in the balance case. The temperature of the stored nitrogen and the water in bottle K were recorded together with the reading of the manometer N. Then the bottle K was weighed.

After the Vanier bulb was weighed, 1.00 ml. of 30% hydrogen peroxide was added to the sodium hydroxide solution in the bulb and nitrogen bubbled through the bulb for 15 minutes. The peroxide oxidized all of the sulfite from the absorbed sulfur dioxide to sulfate. Then the resulting solution was flushed out of the bulb into an excess of 0.1N acid, and the

excess acid back-titrated with 0.2N sodium hydroxide solution to a pH of 7.00. A blank determination was made on the titration procedure; 0.05 ml. of the sodium hydroxide were consumed. Therefore, 0.05 ml. of sodium hydroxide were subtracted from the total volume of sodium hydroxide consumed during the titration.

A sample calculation is now given to illustrate the procedure. The recorded data for run Q-4 is given in Table X. The concentration of the sodium sulfite solution used for this run was 4.745 molal.

TABLE X

RECORDED DATA FOR RUN Q-4

Time	Manometer M, in. water		Manometer N, in. water		Barometer Reading with Temp., °C.		Flow Rate of N_2, bubbles/min.
1010	1.7	10.6	—	—	—		80[a]
1015	1.6	10.7	1.7	—	754.2	22.0	92
1021	1.2	10.1	1.2	—	—		76
1027	1.2	11.1	1.3	—	—		74
1030	2.7	9.6	0.8	--	--		84
1033	2.8	9.5	1.0	—	—		84-98[b]
1040	1.7	10.6	2.0	—	—		88
1100	2.2	10.1	1.2	--	--		70-98[b]
1108	1.8	10.5	2.3	—	754.5	22.0	98
1155	2.3	10.0	1.5	—	—		74-90[b]
1205	1.3	11.0	2.2	—	—		80
1212	2.0	10.3	2.3	—	754.5	22.0	86
1307	2.7	9.6	1.5	7.0	754.5	22.1	76

[a] The values given in this line are averages over the first time interval from 1010 to 1015.

[b] This indicates an instantaneous flow adjustment made at the time indicated.

1) Data recorded before run

Temperature of water in bottle K: 26.3°C.

Volume of 0.2205N NaOH charged to Vanier bulb: 40.00 ml.

Weight of Vanier bulb: tare - 9.0000 + 0.4287 g.

Head of bisulfite solution in sixth equilibrium tube: 1.0 in. water

2) Data recorded after run

Temperature of nitrogen in bottle K: 26.3°C.

Temperature of water in bottle K: 25.9°C.

Weight of water lost from bottle K: 3082 g.

Weight of Vanier bulb: tare - 9.0000 + 0.5882 g.

Volume of 0.09446N HCl used: 100.00 ml.

Volume of 0.2205N NaOH required for back titration: 16.99 ml.

3) Mass of nitrogen passed during run

The mass of nitrogen passed during the run is the mass of nitrogen collected in bottle K. Since the bottle was completely filled with water at the start of the run, the volume of the nitrogen is equal to the volume of bottle K when empty minus the volume of the water in the bottle at the end of the run. Thus,

$$9502 - \frac{(9502)(0.9967) - 3082}{0.9968} = 3092 \text{ ml.}$$

where 9502 = volume of bottle K when empty, ml.;
0.9967 = density of water at 26.3°C.;
0.9968 = density of water at 25.9°C.

The pressure of the nitrogen in bottle K is equal to the atmospheric pressure minus the reading of manometer N at the end of the run minus the vapor pressure of the water in the bottle at the end of the run. It is assumed that Dalton's law of partial pressures is valid in this

case. The atmospheric pressure is determined by correcting the barometric reading for capillarity, scale error and temperature. Thus,

$$751.9 - (7.0 - 1.5)(1.86) - 25.1 = 716.6 \text{ mm. Hg}$$

where 751.9 = corrected barometric pressure, mm. Hg;
1.86 = conversion factor to change in. water to mm. Hg;
25.1 = vapor pressure of water at 25.9°C.

The mass of nitrogen is now calculated from the ideal gas law:

$$\frac{(716.6)(3092)}{(62360)(299.5)} = 0.118635 \text{ moles}$$

where 62360 = gas constant in appropriate units;
299.5 = temperature of the nitrogen, °K.

4) Mass of sulfur dioxide absorbed by Vanier bulb

The mass of sulfur dioxide absorbed by the Vanier bulb is equal to one-half of the number of equivalents of sodium hydroxide consumed. Thus,

$$\frac{(40.00 + 16.99 - 0.05)(0.2205) - (100.00)(0.09446)}{2000} = 0.001555$$

where 0.05 = the blank correction for the titration.

5) Mass of water vapor absorbed by the Vanier bulb

The mass of water vapor absorbed by the Vanier bulb is equal to the total increase in weight of the bulb during the run minus the mass of sulfur dioxide absorbed. It should be noted that the gain or loss of water vapor by the nitrogen stream passing through the sodium hydroxide solution in the Vanier bulb has no effect on this calculation. Thus,

$$\frac{(0.5882 - 0.4287) - (64.07)(0.001555)}{18.016} = 0.003324$$

where 64.07 = molecular weight of sulfur dioxide;
18.016 = molecular weight of water

6) Total pressure of nitrogen stream

The total pressure of the nitrogen stream when in the sixth equilibrium

tube is equal to the atmospheric pressure plus the reading of the manometer M. Since this pressure is continually varying slightly, an average value must be determined. A weighted average pressure is determined by summing the products of the mass of nitrogen passed in each interval of time and the average pressure over that time interval, and dividing this sum by the total mass of nitrogen passed during the run. The mass of nitrogen passed in a time interval is calculated from the number of bubbles per minute and the duration of the time interval. Thus, for the interval from 1155 to 1205, the bubbles of nitrogen passed are

$$\frac{(90 + 80)(10)}{2} = 850 \text{ bubbles}$$

The average pressure of the nitrogen in the equilibrium tube during this time interval is the atmospheric pressure plus the average manometer reading corrected for the head of solution in the sixth equilibrium tube. Thus,

$$751.9 + \left[\frac{(10.0 - 2.3) + (11.0 - 1.3)}{2} - 1.0\right] 1.86 = 766.2 \text{ mm. Hg}$$

When this is done for all of the intervals and the average total pressure calculated as described above, the result is: 756.2 mm. Hg.

7) Vapor pressure of water

The vapor pressure of water above the sodium bisulfite solution is calculated from the definition of partial pressure: the partial pressure of water is equal to the mole fraction of water in the vapor phase times the total pressure. Thus, the vapor pressure of water equals

$$\frac{(0.003324)(756.2)}{0.003324 + 0.001555 + 0.118635} = 20.59 \text{ mm. Hg}$$

8) Vapor pressure of sulfur dioxide

The vapor pressure of sulfur dioxide is evaluated in the same manner as the vapor pressure of water. Thus,

$$\frac{(0.001555)(756.2)}{0.003324 + 0.001555 + 0.118635} = 9.63 \text{ mm. Hg}$$

APPENDIX III

pH MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

The pH of sodium bisulfite solutions was measured as a function of concentration. The measurements were made with a Beckman Model H-2 glass electrode pH meter. The bisulfite solutions were placed in a 50-ml. beaker immersed up to the rim in a constant temperature bath. The bath was controlled at 25.0±0.1°C.

The sodium bisulfite solutions used for the pH measurements were prepared by diluting portions of the same stock bisulfite solution used for the vapor-pressure measurements. Deaerated water stored under nitrogen was used for dilution. The solutions of desired concentration were prepared gravimetrically using an analytical balance. Each solution was prepared in a one-ounce polyethylene bottle; the bottle was filled with the solution to prevent the inclusion of air in the bottle with the solution. Suitable precautions were taken during the dilution procedure to keep the exposure of the solutions to air at a minimum.

The pH measurements were made in the usual manner. The bottles containing the bisulfite solutions were placed in the constant temperature bath for at least 30 minutes before the pH was measured. The pH meter was standardized using a buffer solution of pH 4.00. Then, after the electrodes were warmed slightly with the hand, the solution from one of the bottles in the bath was poured into the beaker. The electrodes and a thermometer were placed in the solution. With practice it was possible to warm the electrodes sufficiently so that the solution was at

the desired temperature immediately after the electrodes were immersed. The solution was stirred with the thermometer and pH reading was recorded.

APPENDIX IV

CALCULATION OF ACTIVITY COEFFICIENTS OF SODIUM SULFITE

The activity coefficients of sodium sulfite in aqueous solutions were calculated from the isopiestic data for sodium sulfite and sodium chloride solutions. The activity-coefficient ratios were calculated from Equation (8) and the value of $\gamma_{1(r)}$ was calculated from the fitted Debye-Hückel equation, Equation (9).

CALCULATION OF ACTIVITY-COEFFICIENT RATIOS

The activity-coefficient ratios of sodium sulfite were calculated from the isopiestic data for sodium sulfite using Equation (8). Because of the uncertainty of isopiestic data obtained on solutions of low concentration, the isopiestic data for sodium sulfite were plotted as the vapor pressure of water above the sodium sulfite solutions versus the mole fraction of water in the solution. This plot became quite linear as the mole fraction of water approached unity and thus the extrapolation to infinite dilution was fairly certain. Comparison of isopiestic data calculated from this plot with the measured isopiestic data indicated that the 0.2 molal isopiestic data point was in error. It should be noted that the values of the isopiestic ratio calculated from such a plot are not sufficiently accurate for extending the experimental isopiestic data to more dilute concentrations; a very small error in the vapor-pressure data produces a large error in the calculated isopiestic ratios. Thus, the activity-coefficient ratios were calculated using both a 0.2 and a 0.4 molal sodium sulfite solution as the solution designated by the

subscript r. The integral of Equation (8) was evaluated by plotting the quantity $(2\underline{m}_R/3\underline{m}_1 - 1)/\sqrt{\underline{a}_{\pm R}}$ versus $\sqrt{\underline{a}_{\pm R}}$ and by calculating the area under the curve using Simpson's rule.

FITTING OF THE DEBYE-HÜCKEL EQUATION

The extended form of the Debye-Hückel equation, Equation (9), was fitted to the activity-coefficient ratio data calculated from Equation (8) using the method of Jones and Dole (26). That is, the constants A and B were adjusted until the equation fit the data. Changing the form of Equation (9) to Briggsian logarithms and substituting in the value of the limiting slope yields

$$\log \gamma = \frac{-1.0165\sqrt{\underline{I}}}{1 + \underline{A}\sqrt{\underline{I}}} + \underline{B}\,\underline{m} \qquad (14)$$

Let $\underline{D} = \log(\gamma_1/\gamma_{1(r)})$, the activity-coefficient ratio calculated from Equation (8). Also, let $\Delta\underline{D} = \underline{D} - \underline{D}_c$ where $\underline{D}_c$ is the value of $\underline{D}$ calculated using Equation (14); that is

$$\underline{D}_c = -\frac{1.0165\sqrt{\underline{I}}}{1 + \underline{A}\sqrt{\underline{I}}} + \underline{B}\,\underline{m} + \frac{1.0165\sqrt{\underline{I}_r}}{1 + \underline{A}\sqrt{\underline{I}_r}} - \underline{B}\,\underline{m}_r \qquad (15)$$

For any given pair of isopiestic solutions $\underline{I}$, $\underline{m}$, $\underline{I}_r$ and $\underline{m}_r$ are fixed and $\underline{D}_c$ is a function of $\underline{A}$ and $\underline{B}$ only. Therefore,

$$\Delta\underline{D} = \frac{\partial \underline{D}_c}{\partial \underline{A}}\Bigg|_{\underline{B}} \Delta\underline{A} + \frac{\partial \underline{D}_c}{\partial \underline{B}}\Bigg|_{\underline{A}} \Delta\underline{B} \qquad (16)$$

carrying out the partial differentiation of Equation (15) as indicated in Equation (16),

$$\Delta\underline{D} = \left(\frac{1.0165\,\underline{I}}{(1 + \underline{A}\sqrt{\underline{I}})^2} - \frac{1.0165\,\underline{I}_r}{1 + \underline{A}\sqrt{\underline{I}_r})^2}\right)\Delta\underline{A} + (\underline{m} - \underline{m}_r)\Delta\underline{B} \qquad (17)$$

The constants $\underline{A}$ and $\underline{B}$ of Equation (14) are evaluated as follows:

1) $\underline{D}_c$ is calculated for each value of $\underline{m}$ using Equation (15) by assuming values of $\underline{A}$ and $\underline{B}$.

2) $\Delta\underline{D}$ is calculated from its definition, $\underline{D} - \underline{D}_c$ for each value of $\underline{m}$.

3) Equation (17) is evaluated for each value of $\underline{m}$; then $\Delta\underline{A}$ and $\Delta\underline{B}$ are calculated from the resulting series of equations by the method of least squares.

4) New values of $\underline{A}$ and $\underline{B}$, $\underline{A}'$ and $\underline{B}'$, are calculated from $\underline{A}' = \underline{A} + \Delta\underline{A}$ and $\underline{B}' = \underline{B} + \Delta\underline{B}$.

5) Steps 1 through 4 are repeated using the new values of $\underline{A}$ and $\underline{B}$ until $\Delta\underline{D}$, $\Delta\underline{A}$ and $\Delta\underline{B}$ are negligibly small.

The Debye-Hückel equation was fitted using both 0.2 and 0.4 as the molality of the solution designated with subscript r. The equation was fitted for even values of the molality up to 1.0. Difficulty was encountered when the equation was fitted using the 0.2 molal solution. The values of $\Delta\underline{D}$, $\Delta\underline{A}$ and $\Delta\underline{B}$ were minimized by the calculation procedure; however, these minimum values were not negligibly small. It was evident from a plot of the series of equations resulting from Equation (17) that the equations for the most dilute solutions did not fit into the pattern of the other equations. However, the fitting of the equation to the data using the 0.4 molal solution was very satisfactory; the quantities $\Delta\underline{D}$, $\Delta\underline{A}$ and $\Delta\underline{B}$ were readily reduced to negligible quantities. On the basis of this result and the previous indication of the unreliability of the 0.2 molal isopiestic data point, the 0.2 molal data point was discarded and the fitted Debye-Hückel equation using the 0.4 molal solution was accepted. An attempt was made to fit the Debye-Hückel equation over

the concentration range from 0.4 to 1.4 molal. The result was similar to the result when the 0.2 molal solution was used for the calculation--the values of ΔD, ΔA and ΔB could not be reduced to negligible values. It was then concluded that the Debye-Hückel equation could not represent the activity coefficient data much above a concentration of 1.0 molal.

The fitted Debye-Hückel equation was used to evaluate the activity coefficient of sodium sulfite in a 0.4 molal solution. Also, the values of the activity coefficients of sodium sulfite for solutions below 0.4 molal that appear in Table V were calculated from this equation. A sample calculation is given to illustrate the calculation procedure.

Molality of solution designated by the subscript r: 0.4

Molality of solution designated by subscript 1: 0.7

Value of activity coefficient ratio D calculated from Equation (8):

$$D = \log (\gamma_1/\gamma_{1(r)}) = -0.07654$$

Assumed values of A and B: 0.93 and 0.001, respectively.

Value of D_c calculated from Equation (15):

$$D_c = -\frac{(1.0165)\sqrt{(3)(0.7)}}{1 + (0.93)\sqrt{(3)(0.7)}} + (-0.001)(0.7)$$

$$+ \frac{(1.0165\sqrt{(3)(0.4)}}{1 + (0.93)\sqrt{(3)(0.4)}} = (-0.001)(0.4) = -0.07623$$

Value of ΔD calculated from its definition, $D - D_c$:

$$\Delta D = -0.07654 - (-0.07623) = -0.00031$$

Evaluation of Equation (17):

$$\Delta D = -0.00031 = \left(\frac{(1.0165)(3)(0.7)}{[1 + 0.93\sqrt{(3)(0.7)}]^2} - \frac{(1.0165)(3)(0.4)}{[1 + 0.93\sqrt{(3)(0.4)}]^2}\right)\Delta A + (0.7 - 0.4)\Delta B$$

or $$-0.00103 = 0.29307\Delta\underline{A} + \Delta\underline{B}$$

Values of $\Delta\underline{A}$ and $\Delta\underline{B}$ calculated from the series of equations for $\Delta\underline{A}$ and $\Delta\underline{B}$ by the method of least squares:

$$\Delta\underline{A} = 0.0744; \quad \Delta\underline{B} = -0.0236$$

New values of $\underline{A}$ and $\underline{B}$:

$$\underline{A}' = 0.93 + 0.0744 = 1.004$$

$$\underline{B}' = -0.001 - 0.0236 = -0.0246$$

Final values of $\Delta\underline{D}$, $\Delta\underline{A}$ and $\Delta\underline{B}$ after calculation procedure was repeated three times:

$$\Delta\underline{D} = 0.00006; \quad \Delta\underline{A} = 0.00085; \quad \Delta\underline{B} = 0.0001$$

Final values of $\underline{A}$ and $\underline{B}$:

$$\underline{A} = 1.0310; \quad \underline{B} = -0.0295$$

Value of $\gamma_{1(r)}$ calculated from Equation (14): 0.2920

Value of γ_1 calculated from $\underline{D}$: 0.2448

CALCULATION OF DEGREE OF HYDROLYSIS

The degree of hydrolysis can be calculated in the following manner. The equation for the hydrolysis of sulfite ions in a sodium sulfite solution is

$$SO_3^= + H_2O = HSO_3^- + OH^- \tag{18}$$

The equilibrium constant or hydrolysis constant for this reaction is

$$\underline{K}_H = \frac{\underline{a}_{HSO_3^-}\,\underline{a}_{OH^-}}{\underline{a}_{SO_3^=}\,\underline{a}_w} = \frac{\underline{m}_1\underline{x}\gamma_{HSO_3^-}\,\underline{m}_1\underline{x}\gamma_{OH^-}}{\underline{m}_1(1-\underline{x})\gamma_{SO_3^=}\,\underline{a}_w} \tag{19}$$

where $\underline{x}$ = the degree of hydrolysis—the fraction of the sulfite ions that are hydrolyzed.

It is readily shown that $\underline{K}_H$ is equal to the ratio of the ionization

constant of water and the second ionization constant of sulfurous acid. At 25°C. $\underline{K}_H$ has a value of 1.60×10^{-7}.

Introducing a new quantity $\underline{k}$ defined as

$$\underline{k} = \underline{K}_H \gamma_{SO_3^=} / \gamma_{HSO_3^-} \gamma_{OH^-} \tag{20}$$

Equation (19) can be rewritten as

$$\underline{k} = \underline{m}_1 \underline{x}^2 / (1 - \underline{x}) \tag{21}$$

It can be shown from the Debye-Hückel equation that, at infinite dilution, the following relationships are valid:

$$\left.\begin{aligned} \sqrt[4]{\gamma_{SO_3^=}} &= \gamma_{Na^+} \\ \gamma_{HSO_3^-} &= \gamma_{Na^+} \end{aligned}\right\} \tag{22}$$

It follows then from the definition of mean ionic activity coefficient that

$$\left.\begin{aligned} \sqrt{\gamma_{SO_3^=}} &= \gamma_1 \\ \gamma_{HSO_3^-} &= \gamma_2 \end{aligned}\right\} \tag{23}$$

Substituting the relationships of Equations (23) into Equation (20) yields (assuming γ_{OH^-} equals $\gamma_{HSO_3^-}$)

$$\underline{k} = \underline{K}_H \ \gamma_1^2 / \gamma_2^2 \tag{24}$$

The quantity $\underline{k}$ can be evaluated from Equation (24) since all of the quantities in this equation can be evaluated for a given value of $\underline{m}$.

Therefore, the degree of hydrolysis $\underline{x}$ can be calculated from Equation (21) using the quadratic formula:

$$\underline{x} = -\underline{k}/2\underline{m}_1 + \sqrt{(\underline{k}/2\underline{m}_1)^2 + \underline{k}/\underline{m}_1} \qquad (25)$$

This equation is strictly valid at infinite dilution only; it is not known how well these relationships hold as the concentration is increased.

For $\underline{m}_1$ equal to 0.4, the degree of hydrolysis calculated from Equation (25) is 0.00024. The degree of hydrolysis decreases with increasing concentration. At $\underline{m}_1$ equal to 0.1, the calculated degree of hydrolysis is 0.001; at $\underline{m}_1$ equal to 2.0, the calculated degree of hydrolysis is 0.00007.

APPENDIX V

COMPOSITION OF SODIUM BISULFITE SOLUTIONS

The composition of sodium bisulfite solutions was calculated by solving the equilibrium equation, Equation (3), together with the sodium balance equation, Equation (4). Equations (3) and (4) were combined by eliminating m_2 from both equations and the resulting equation was arranged in the following form:

$$\frac{K\gamma_1^3 a_S\, a_w}{\gamma_2^4} = \frac{(m_{Na} - 2m_1)^2}{m_1} \qquad (26)$$

Equation (26) was solved by trial and error. A value of m_{Na} was chosen; the values of the quantities on the left side of the equation were then evaluated for this value of m_{Na}. To evaluate the activity coefficients, the total ionic strength was assumed equal to m_{Na}. A value of m_1 was assumed and the right side of the equation was evaluated. The value of m_1 was varied until both sides of the equation were equal. Then the total ionic strength was calculated and, when necessary, the activity coefficients were re-evaluated, etc., until there was no further change in the values of the activity coefficients. This procedure was followed for each value of m_{Na} desired. The calculations were made with the aid of an IBM 610 computer. The value of m_1 could not be solved directly using the quadratic formula because the form of the formula yielded m_1 as the difference of two relatively large numbers.

The pH of sodium bisulfite solutions can be calculated from three equations:

$$\underline{a}_{H^+} = \underline{K}_1 \underline{a}_S \underline{a}_w/\gamma_2 \underline{m}_2 \qquad (27)$$

$$\underline{a}_{H^+} = \underline{K}_2 \gamma_2 \underline{m}_2/\gamma_1^2 \underline{m}_1 \qquad (28)$$

$$\underline{a}_{H}^{2+} = \underline{K}_1 \underline{K}_2 \underline{a}_S \underline{a}_w/\gamma_1^2 \underline{m}_1 \qquad (29)$$

The first two of these equations are derived from the equations for the ionization constants of sulfurous acid utilizing the relationships given in Equation (23). The relationships given by Equation (23) are strictly valid only at infinite dilution; it is not known how well these relationships hold as the concentration is increased. Equation (29) is derived by eliminating the activity of the bisulfite ion from the other two equations. The pH was calculated from all three equations with the resulting pH values being, respectively: 4.21 ± 0.06; 4.45 ± 0.08; 4.33 ± 0.08. The values after the plus and minus signs are equal to the standard errors.

APPENDIX VI

COMPOSITION OF SODIUM SULFITE-BISULFITE SOLUTIONS

The composition of the various sodium sulfite-bisulfite solutions cannot be calculated because only qualitative sulfur dioxide vapor-pressure data are available. However, the composition can be approximated by qualitative reasoning. It is known that as the ratio of total sulfur dioxide to total sodium decreases from 1.0 to 0.5, the vapor pressure of sulfur dioxide decreases in the manner described on page 57. Therefore, the activity of sulfur dioxide must also decrease proportionately.

It can be shown from Equation (26) that the activity of sulfur dioxide must decrease about ninetyfold when the total sulfur dioxide to total sodium ratio is 0.9 and the molality of total sodium is 0.1 in order to have even the stoichiometric ratio of sodium sulfite to sodium bisulfite present. Also, the pH of the sulfite-bisulfite solutions increases as the ratio of total sulfur dioxide to total sodium decreases from 1.0 toward 0.5. Since the pH is a measure of the ionization of the dissolved sulfur dioxide, the ionization of the dissolved sulfur dioxide must decrease proportionately. Therefore, the concentration of dissolved sulfur dioxide can be assumed approximately equal to the molality of the sodium sulfite from the dissociated sodium bisulfite when the ratio of total sulfur dioxide to total sodium is less than 0.9.

It can be concluded then, from a consideration of Equation (2), that since the activity of sulfur dioxide decreases ninetyfold, the

molality of the sodium sulfite from the dissociation of sodium bisulfite must decrease proportionately. (This is true providing the activity coefficient of the dissolved sulfur dioxide is independent of the ratio of total sulfur dioxide to total sodium.) The dissociation of sodium bisulfite in a sodium bisulfite solution when the molality of total sodium is 0.1 is about 0.8%. Therefore, it is believed that the bisulfite dissociation is less than 0.1% for sulfite-bisulfite solutions when the ratio of total sulfur dioxide to total sodium is 0.9 and the molality of total sodium is 0.1. The vapor pressure of sulfur dioxide above a sulfite-bisulfite solution when the total sulfur dioxide to total sodium ratio is 0.95 was estimated to be about twice as high as when the ratio is 0.9. Therefore, the dissociation of bisulfite is assumed to be about twice the dissociation when the ratio is 0.9, or less than 0.2%. Also, since the bulk of the increase in the vapor pressure of sulfur dioxide above sulfite-bisulfite solutions occurs when the ratio of total sulfur dioxide to total sodium is between 0.95 and 1.0, it can be assumed with some confidence that the bulk of the increase in dissociation of bisulfite occurs simultaneously. The dissociation of bisulfite decreases with increasing concentration in the case of sodium bisulfite solutions; thus, it is assumed that the same phenomenon will occur when the ratio of total sulfur dioxide to total sodium is less than 1.0.

APPENDIX VII

SUPPLEMENTARY DISCUSSION OF CALCULATED RESULTS

ACTIVITY OF SULFUR DIOXIDE IN SULFITE-BISULFITE SOLUTIONS

If it is assumed that the molalities of sodium sulfite and sodium bisulfite in the various sulfite-bisulfite solutions are equal to the stoichiometric concentrations, then the activity of sulfur dioxide can be calculated from Equation (26). This was done for values of the ratio of total sulfur dioxide to total sodium of 0.9 and 0.8. The results are shown in Fig. 11. The broken horizontal lines on the graph show plus and minus one standard deviation of the average of the horizontal portion of each curve. The standard error in each case is about 27%.

Since the standard error is so large, it is doubted that the decrease in the activity of sulfur dioxide at the high concentrations is significant. Since the vapor pressure of sulfur dioxide is directly proportional to the sulfur dioxide activity, the vapor pressure of sulfur dioxide above the solutions decreases at the high concentrations also. This decrease of sulfur dioxide vapor pressure did not occur in the case of sodium bisulfite solutions. A decrease in the sulfur dioxide activity could occur if the equilibrium expressed by Equation (2) was displaced further to the right or the activity coefficient of the dissolved sulfur dioxide changed considerably.

ACTIVITY COEFFICIENT OF DISSOLVED SULFUR DIOXIDE

It is possible to estimate the activity coefficient of the dissolved sulfur dioxide in a sodium bisulfite solution. Assuming that the molality

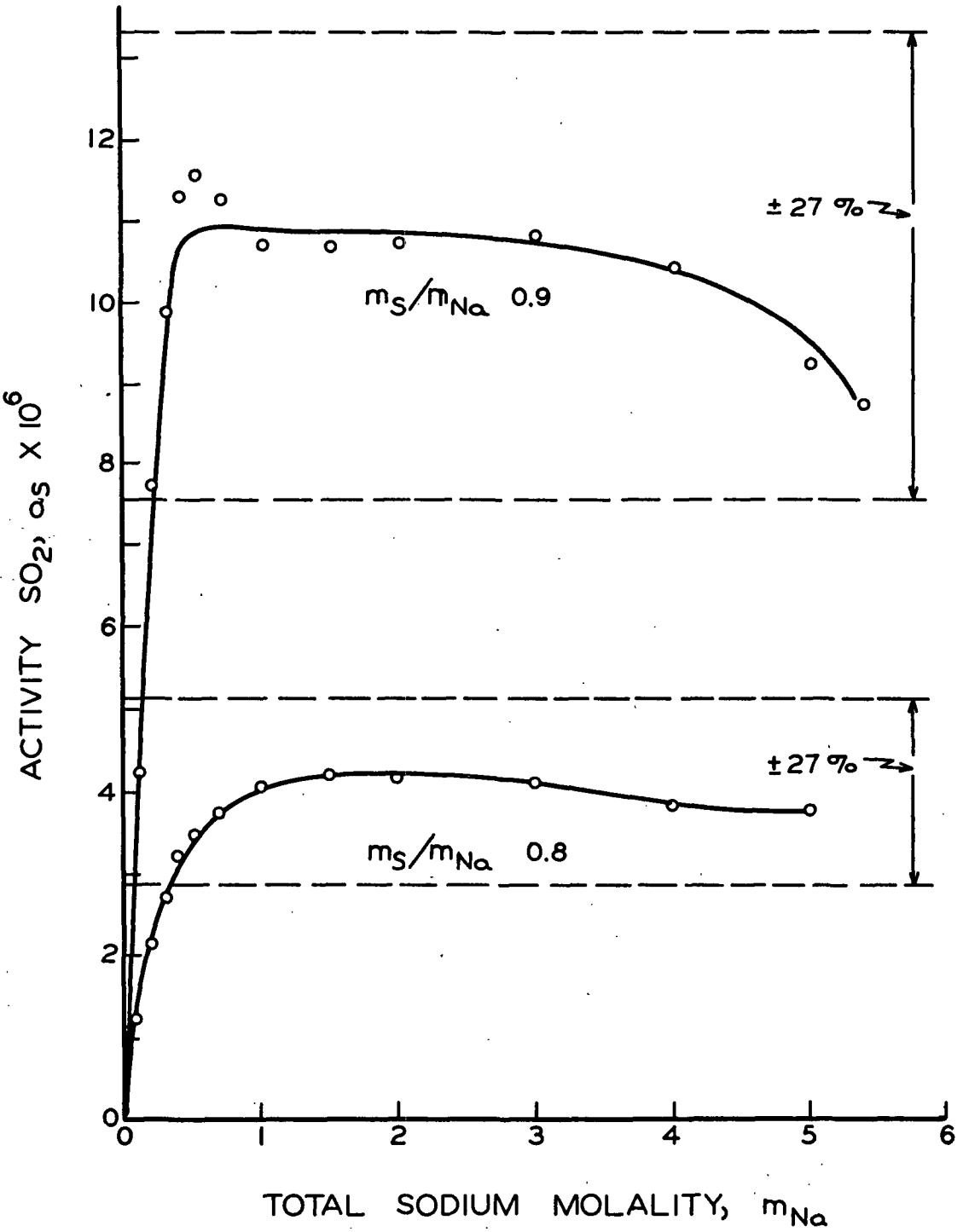

Figure 11. Activity of SO_2 in Na_2SO_3-$NaHSO_3$ Solutions at 25°C.

of the dissolved sulfur dioxide is equal to the molality of the sodium sulfite in the solution, the activity coefficient of dissolved sulfur dioxide can be calculated from the activity of sulfur dioxide. The calculations showed that the activity coefficient is about unity up to a molality of about 0.2 and then increases fairly linearly until at a molality of 6, it is about 25. The standard error of the calculated activity coefficient is about 18%.

CONVERGENCE OF ACTIVITY-COEFFICIENT DATA FOR SODIUM SULFITE-BISULFITE SOLUTIONS

The convergence of the activity-coefficient data for sodium sulfite and sodium bisulfite in sodium sulfite-bisulfite solutions at a total ionic strength of about 0.5 has already been discussed in relation to the well-known Lewis and Randall assumption. It is interesting to note further that there is no trend in the data from which the activity-coefficient data were calculated that indicates that the convergence exists. However, it is evident that the rate of change of the slopes of the curves of Figs. 9 and 11 is greatest in the same range of values of the molality of total sodium in which the convergence occurs. This, of course, indicates that the thermodynamic nature of the sulfite-bisulfite system changes rapidly in that range of values of the molality of total sodium.

pH OF SODIUM BISULFITE SOLUTIONS

The pH data for sodium bisulfite solutions reported in the literature, (19) and (20), show that a plot of the pH versus molality goes through a sharp minimum at about 0.05 molal and a maximum at about 0.35

molal. The difference between the value of the pH at the minimum and the maximum is about one pH unit--meaning of course a tenfold change in the hydrogen ion activity. Figure 4 shows that the pH data obtained in this study do not show any evidence of such a phenomenon; it can be shown that this phenomenon is thermodynamically inconsistent.

The pH of a sodium bisulfite solution can be calculated from Equations (27), (28), and (29). Even though the values of pH calculated from these equations are only approximate when the concentration is increased from infinite dilution, the functional relationship should still be generally the same. The values of the pH calculated from Equation (28) for molalities from 0.1 to 0.65 all lie on a smooth curve without maxima or minima; this curve does not differ significantly from the curve of the measured pH values over the range of molality from 0.1 to 0.3. It was estimated from Equation (28) that abrupt changes in the activity-coefficient data of the order of 50% would be necessary in order to produce the variation in the pH data observed by the other workers. This amount of variation is extremely unlikely, especially in these dilute solutions. Hence, it is concluded that the pH data reported by these other workers are thermodynamically inconsistent.

APPENDIX VIII

DERIVATION OF THERMODYNAMIC RELATIONSHIPS

THE EQUILIBRIUM EQUATION

The equilibrium constant for Equation (2) is defined as

$$\underline{K} = \frac{\underline{a}_2^2}{\underline{a}_1 \, \underline{a}_S \, \underline{a}_W} \tag{30}$$

The definition of the mean ionic activity, $\underline{a}_{\pm}$, is

$$\underline{a} = \underline{a}_{\pm}^{\nu} = (\gamma \underline{m}_{\pm})^{\nu} \tag{31}$$

where $\nu = \nu_+ + \nu_-$, the sum of the number of cations and anions, respectively, produced by the complete dissociation of one molecule of electrolyte;

$\underline{m}$ = the mean ionic molality defined by

$$\underline{m}_{\pm} = (\underline{m}_+^{\nu_+} \, \underline{m}_-^{\nu_-})^{1/\nu} \tag{32}$$

Thus, in Equation (30), the value of $\underline{a}_2$ becomes

$$\underline{a}_2 = \underline{a}_{\pm 2}^2 = \gamma_2^2 \, \underline{m}_{\pm 2}^2 = \gamma_2^2 \, \underline{m}_{Na} \, \underline{m}_2 \tag{33}$$

and the value of $\underline{a}_1$ becomes

$$\underline{a}_1 = \underline{a}_{\pm 1}^3 = \gamma_1^3 \, \underline{m}_{\pm 1}^3 = \gamma_1^3 \, \underline{m}_{Na}^2 \, \underline{m}_1 \tag{34}$$

since

$$\underline{m}_{Na} = 2 \, \underline{m}_1 + \underline{m}_2 \tag{4}$$

When the values of $\underline{a}_1$ and $\underline{a}_2$ from Equations (33) and (34) are substituted in Equation (30), the result is Equation (3):

$$\underline{K} = \frac{\gamma_2^4 \, \underline{m}_2^2}{\gamma_1^3 \, \underline{m}_1 \, \underline{a}_S \, \underline{a}_W} \tag{3}$$

The equilibrium constant can be shown to be equal to $\underline{K}_1/\underline{K}_2$ by writing the equilibrium equations for the ionization constants and introducing the definition of the mean ionic activity, $\underline{a} = \underline{a}_{\pm}^{\nu} = \underline{a}_{+}^{\nu+}\underline{a}_{-}^{\nu-}$.

INTEGRATED FORM OF GIBBS-DUHEM EQUATION

The differential form of the Gibbs' free energy equation for a phase of a system containing $\underline{c}$ components at constant temperature and pressure is

$$d\underline{F} = \mu_1\, d\underline{n}_1 + \mu_2\, d\underline{n}_2 + \cdots \mu_{\underline{c}}\, d\underline{n}_{\underline{c}} = \sum_{1}^{\underline{c}} \mu_i\, d\underline{n}_i \qquad (35)$$

where $\underline{F}$ = Gibbs' free energy;
μ = chemical potential;
$\underline{n}$ = number of moles.

The chemical potential of component 1 is defined by

$$\mu_1 = \left.\frac{\partial \underline{F}}{\partial \underline{n}_1}\right| P, T, \underline{n}_2 \cdots \underline{n}_{\underline{c}} \qquad (36)$$

Similar definitions can be written for the other components.

Equation (35) can be integrated to yield:

$$\underline{F} = \mu_1\, \underline{n}_1 + \mu_2\, \underline{n}_2 + \cdots \mu_{\underline{c}}\, \underline{n}_{\underline{c}} = \sum_{1}^{\underline{c}} \mu_i\, \underline{n}_i \qquad (37)$$

If the complete differential of Equation (37) is written,

$$d\underline{F} = \sum_{1}^{\underline{c}} \mu_i\, d\underline{n}_i + \sum_{1}^{\underline{c}} \underline{n}_i\, d\mu_i \qquad (38)$$

and combined with Equation (35), the result is

$$\sum_{1}^{c} \underline{n}_i \, d\mu_i = 0 \qquad (39)$$

The activity, $\underline{a}_i$, of a constituent of a solution is defined by

$$\mu_i = \mu_i^{\circ} + R\,T\,d\,\ln \underline{a}_i \qquad (40)$$

where μ_i° is the chemical potential in some arbitrary standard state. When Equation (40) is combined with Equation (39) and the number of moles of each constituent converted to a molality basis, the result is a form of the well-known Gibbs-Duhem equation,

$$\sum_{1}^{c} \underline{m}_i \, d \ln \underline{a}_i = 0 \qquad (41)$$

Application of the Gibbs-Duhem equation to isopiestic sodium sulfite and sodium chloride solutions yields:

$$\underline{m}_1 \, d \ln \underline{a}_1 + \underline{m}_w \, d \ln \underline{a}_w = 0 \qquad (5)$$

$$\underline{m}_R \, d \ln \underline{a}_R + \underline{m}_w \, d \ln \underline{a}_w = 0 \qquad (6)$$

The second term in each of these equations is identical since the activities of water in two isopiestic solutions are equal. If equations (5) and (6) are thus combined and the relationships analogous to Equations (33) and (34) are substituted into the resulting equation, the final equation is

$$\underline{m}_1 \, d \ln(\gamma_1 \sqrt[3]{4\underline{m}_1})^3 - \underline{m}_R \, d \ln(\gamma_R \underline{m}_R)^2 = 0 \qquad (42)$$

When this equation is solved for $d \ln \gamma_1$, the quantity $d \ln(\gamma_R \underline{m}_R)$ added to both sides of the resulting equation, and the final equation rearranged, the result is

$$d \ln\gamma_1 = d \ln\gamma_R + d \ln(\underline{m}_R/\underline{m}_1) + \left(\frac{2\underline{m}_R}{3\underline{m}_1} - 1\right) d \ln(\gamma_R \underline{m}_R) \qquad (43)$$

When $d \ln(\gamma_R \underline{m}_R) = (2\, d\sqrt{\underline{a}_{\pm,R}})/\sqrt{\underline{a}_{\pm,R}}$ is substituted into this equation and the resulting equation is integrated from infinite dilution to any finite concentration, the final result is Equation (7):

$$\ln\gamma_1 = \ln\gamma_R + \ln(2\underline{m}_R/\underline{m}_1) + 2\int_0^{\underline{a}_{\pm R}} (\frac{2\underline{m}_R}{3\underline{m}_1} - 1) \frac{d\sqrt{\underline{a}_{\pm,R}}}{\sqrt{\underline{a}_{\pm,R}}} \qquad (7)$$

When Equation (43) is integrated from some dilute concentration designated by the subscript r, the result is Equation (8):

$$\ln(\gamma_1/\gamma_{1\,(r)}) = \ln(\gamma_R/\gamma_{R\,(r)}) + \ln\frac{\underline{m}_R/\underline{m}_1}{(\underline{m}_R/\underline{m}_1)_r} + 2\int_{\underline{a}_{\pm,R\,(r)}}^{\underline{a}_{\pm R}} (\frac{2\underline{m}_R}{3\underline{m}_1} - 1) \frac{d\sqrt{\underline{a}_{\pm,R}}}{\sqrt{\underline{a}_{\pm,R}}} \qquad (8)$$

THE DEBYE-HÜCKEL EQUATION

The basic Debye-Hückel equation, derived from consideration of the statistical distribution of ions in solution and the electrostatic attractive forces acting between the ions in solution, is

$$\ln\gamma = -\underline{b}\sqrt{\underline{I}} \qquad (44)$$

This equation describes activity-coefficient data only in very dilute solutions. The equation has been modified by the addition of more terms so that the equation can describe activity-coefficient data over a wider

range of concentration. One extended form of Equation (44) that has been widely used is

$$\ln\gamma = \frac{b\sqrt{I}}{1 + A\sqrt{I}} + B\,m \tag{9}$$

THE McKAY-PERRING EQUATION

The McKay-Perring equation is derived from the Gibbs' free energy equation, Equation (35). The condition of integration of Equation (35) requires that it be a smooth, continuous function. Therefore, partial relationships like the following can be written:

$$\left.\frac{\partial \ln a_1}{\partial n_w}\right|_{n_1,n_2} = \left.\frac{\partial \ln a_w}{\partial n_1}\right|_{n_2,n_w} \tag{45}$$

A similar equation can be written for a sodium sulfite-bisulfite solution in terms of molalities with the ratio, m_1/m_2, and a_w as the independent variables:

$$\left.\frac{\partial \ln a_1}{\partial(m_w/m_2)}\right|_{m_1/m_2} = \left.\frac{\partial \ln a_w}{\partial(m_1/m_2)}\right|_{m_w/m_2} \tag{46}$$

If both sides of this equation are multiplied by

$$\left.\frac{\partial(1/m_2)}{\partial \ln a_w}\right|_{m_1/m_2}$$

the following result can be obtained

$$\left.\frac{\partial \ln a_1}{\partial \ln a_w}\right|_{m_1/m_2} = -55.51 \left.\frac{\partial(1/m_2)}{\partial(m_1/m_2)}\right|_{a_w} \tag{47}$$

where 55.51 = molality of water, m_w.

If $\underline{m}_1/\underline{m}_2$ is held constant, it can be readily shown that

$$d \ln \underline{a}_1 = 3 \, d \ln(\underline{I}\gamma_1) \tag{48}$$

Let $\underline{x}_1 = \underline{I}_1/\underline{I}$ and $\underline{x}_2 = \underline{I}_2/\underline{I}$; introducing these definitions and Equation (48) into Equation (47):

$$\left.\frac{3\,\partial \ln(\underline{I}\gamma_1)}{\partial \ln \underline{a}_w}\right|_{\underline{x}_1} = -55.51 \left[3/\underline{I}^2\left(\frac{\partial \underline{I}}{\partial \ln \underline{x}_2}\right)_{\underline{a}_w} + 3/\underline{I}\right] \tag{49}$$

The Gibbs-Duhem equation written for an isopiestic reference solution of sodium chloride is

$$\frac{2 \, d \ln(\underline{I}_R\gamma_R)}{d \ln \underline{a}_w} = -55.51(1/\underline{I}_R) \tag{50}$$

Subtracting Equation (50) from Equation (49) yields

$$3 \, d \ln(\underline{I}\gamma_1) = 2 \, d \ln(\underline{I}_R\gamma_R) - 55.51\left[3/\underline{I}^2\left(\frac{\partial \underline{I}}{\partial \ln \underline{x}_2}\right)_{\underline{a}_w} + 3/\underline{I} - 1/\underline{I}_R\right] d \ln \underline{a}_w \tag{51}$$

Equation (51) is modified following the suggestions of Bonner and Holland by substituting $\partial \ln \underline{x}_2 = \partial \underline{x}_2/\underline{x}_2$ and $\partial \underline{x}_1 = -\partial \underline{x}_2$ into the equation:

$$3 \, d \ln(\underline{I}\gamma_1) = 2 \, d \ln(\underline{I}_R\gamma_R) - 55.51\left[3\,\underline{x}_2\left(\frac{\partial(1/\underline{I})}{\partial \underline{x}_1}\right)_{\underline{a}_w} + 3/\underline{I} - 1/\underline{I}_R\right] d \ln \underline{a}_w \tag{52}$$

Equation (52) can be integrated to give:

$$3 \ln(\underline{I}\gamma_1) = 2 \ln(\underline{I}_R\gamma_R) - 55.51 \int_1^{\underline{a}_w}\left[3\,\underline{x}_2\left(\frac{\partial(1/\underline{I})}{\partial \underline{x}_1}\right)_{\underline{a}_w} + 3/\underline{I} - 1/\underline{I}_R\right] d \ln \underline{a}_w \tag{53}$$

The constant of integration of Equation (53) is shown to be equal to zero by the Gibbs-Duhem equation. Equation (53) can be used to calculate the activity coefficient of sodium sulfite in sulfite-bisulfite solutions. An equivalent equation can be written for the activity coefficient of sodium bisulfite by interchanging the subscripts 1 and 2. When this is done, Equation (11) in the text is the result. Equation (54) can also be integrated from some finite concentration designated by the subscript r. When this is done, Equation (12) in the text is the result.

APPENDIX IX

DENSITY MEASUREMENTS ON SODIUM BISULFITE SOLUTIONS

In the course of the experimental work, the density of sodium bisulfite solutions was measured as a function of the molality of total sodium in the solutions. A standard pycnometric method was used with the temperature controlled at 25.000±0.005°C. The results are given in Table X. The values of the density are the mean of two determinations; the maximum difference observed between a pair of the density measurements was less than 0.005%. It is believed that the accuracy of the density measurements is better than 0.01%.

TABLE XI

Molality $NaHSO_3$	Density, g./ml.
0.2257	1.0124
0.3634	1.0220
0.5723	1.0353
0.7119	1.0442
0.7211	1.0449
1.048	1.0650
1.943	1.1166
4.745	1.2457
7.0147	1.3364